

Supporting Information

for

Chiral multifunctional thiourea-phosphine catalyzed asymmetric [3 + 2] annulation of Morita–Baylis–Hillman carbonates with maleimides

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Experimental procedures and characterization data of compounds given in this article

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General remarks:

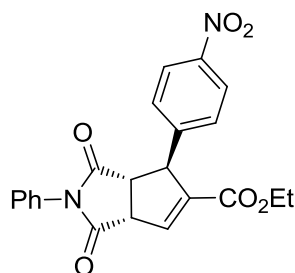
Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$ -values are given in units of $10 \text{ deg}^{-1} \text{ cm}^2 \text{ g}^{-1}$. ^1H NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrometer for solution in CDCl_3 with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hertz. ^{13}C NMR spectra were recorded on a Bruker AM-300 and AM-400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers (CDCl_3 : 77.0 ppm). ^{31}P NMR spectra were recorded on a Bruker AM-400 spectrophotometers (161.9 MHz) for solution in CDCl_3 with 85% H_3PO_4 as an internal standard; infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Flash column chromatography was performed with 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H, and IC-H columns $4.6 \times 250 \text{ mm}$, (Daicel Chemical Ind., Ltd.)) and chiral column (Phenomenex Lux 5μ Amylose-2 column $4.6 \times 250 \text{ mm}$ (PA-2, (Phenomenex Ind., Ltd.)). Mass spectra were recorded by EI, ESI, MALDI and HRMS, measured on a HP-5989 instrument.

1. General procedure for asymmetric [3 + 2] annulation.

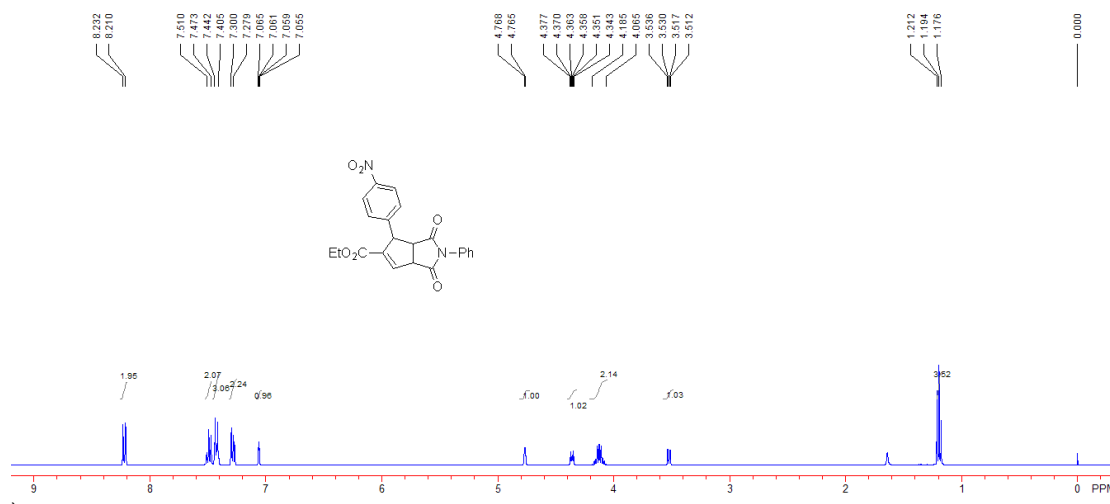
Catalyst **TP** was synthesized according to the literature [1], and its yield, characterization and spectra are provided in [1].

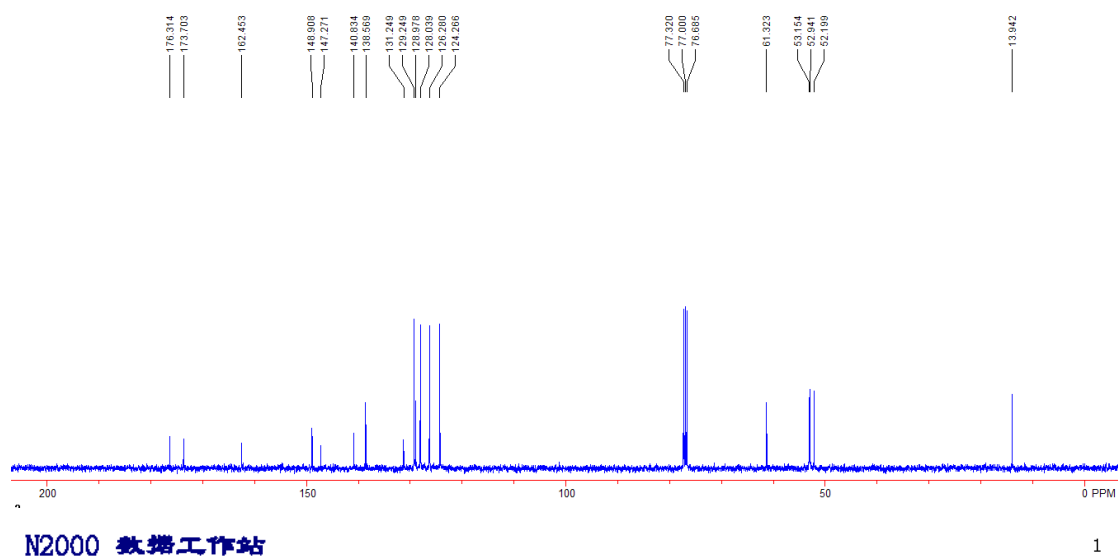
General Procedure for Asymmetric [3 + 2] Annulation:

Under an argon atmosphere, a mixture of maleimide **1** (0.2 mmol), MBH carbonate **2** (0.2 mmol) and catalyst **TP** (0.02 mmol, 11 mg) in toluene (1.0 mL) was stirred at room temperature for 24–48 h. Then the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (elution with petroleum ether/EtOAc 10:1–4:1) to provide compound **3**.



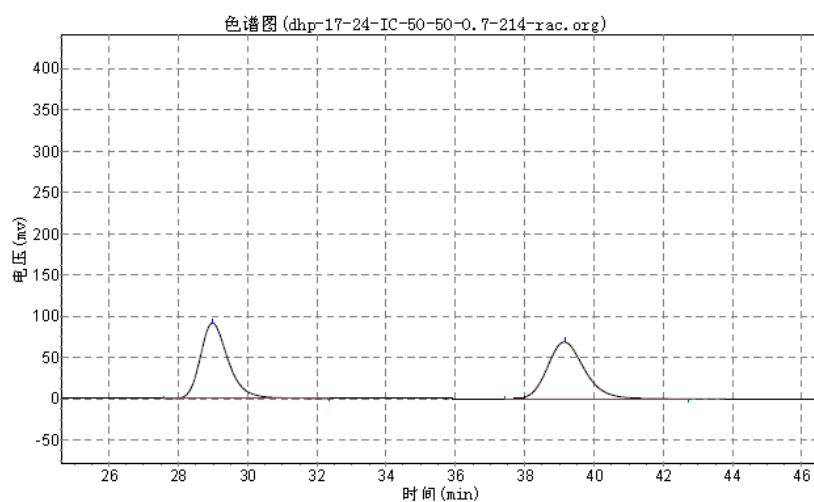
(3aR,4S,6aS)-ethyl 4-(4-nitrophenyl)-1,3-dioxo-2-phenyl-1,2,3,3a,4,6a-hexahydro-cyclopenta[c]pyrrole-5-carboxylate (3a). Yield: 30 mg, 74%; yellow oil; IR (CH₂Cl₂): ν 3076, 2981, 1779, 1716, 1635, 1597, 1519, 1496, 1456, 1348, 1273, 1181, 1089, 1053, 1014, 988, 889, 852, 814, 769, 752, 734, 692, 661 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.19 (3H, t, J = 7.2 Hz, CH₃), 3.52 (1H, dd, J = 2.4, 7.2 Hz, CH), 4.06–4.18 (2H, m, CH₂), 4.34–4.38 (1H, m, CH), 4.77 (1H, d, J = 1.2 Hz, CH), 7.06 (1H, dd, J = 1.6, 2.4 Hz, CH), 7.28–7.30 (2H, m, ArH), 7.40–7.44 (3H, m, ArH), 7.47–7.51 (2H, m, ArH), 8.22 (2H, d, J = 8.8 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.9, 52.2, 52.9, 53.2, 61.3, 124.3, 126.3, 128.0, 129.0, 131.2, 138.6, 140.8, 147.3, 148.9, 162.4, 173.7, 176.3; MS (ESI) m/z (%): 407.0 (100) [M⁺ + 1]; HRMS (ESI) Calcd. for C₂₂H₁₈N₂NaO₆ (M⁺ + Na) requires 429.1057, found: 429.1062; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 214 nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; t_{major} = 28.13 min, t_{minor} = 38.19 min; ee = 96%; [α]_D²⁰ = +383.9 (c 1.0, CHCl₃)].





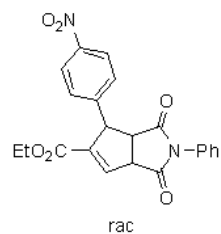
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积分方法: 面积归一法



分析结果表

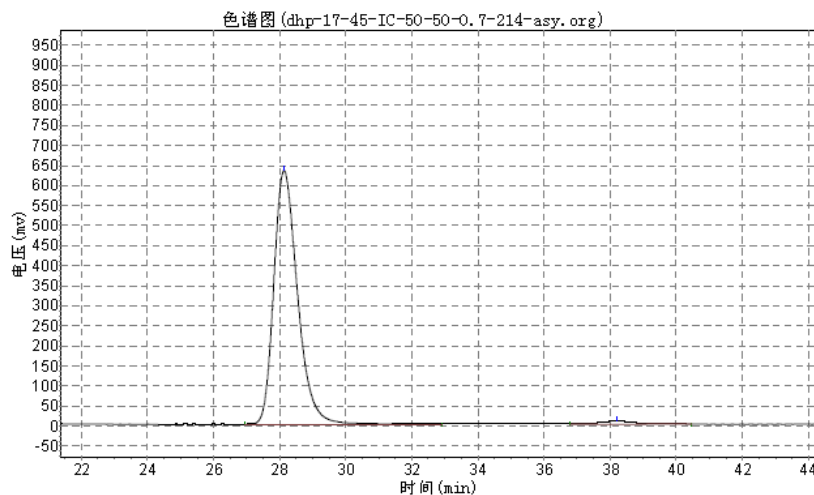
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IC-H, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

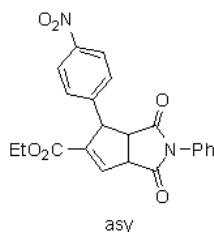
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积分方法: 面积归一法



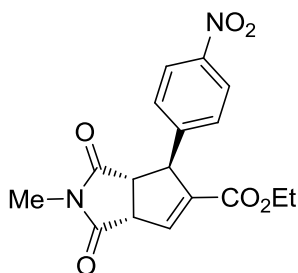
分析结果表

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2		38.193	8477.035	601178.625	1.8671
总计			641557.848	32199146.625	100.0000



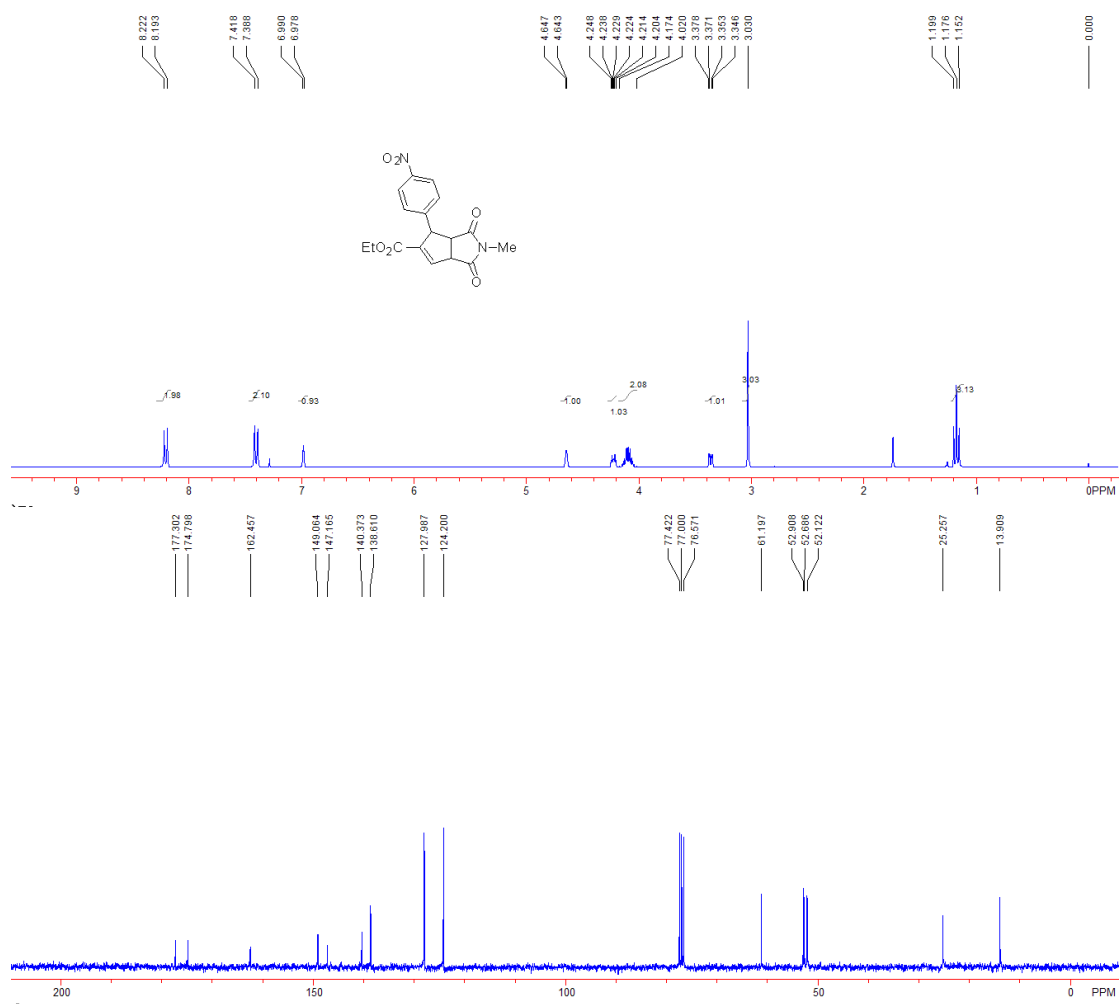
IC-H, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 28.13$ min, $t_{\text{minor}} = 38.19$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +338.9$ (c 1.0, CHCl_3)].



(3aR,4S,6aS)-ethyl 2-methyl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3b). Yield: 34 mg, 99%; yellow oil; IR (CH_2Cl_2): ν 2983, 1782,

1704, 1635, 1597, 1519, 1494, 1434, 134, 1273, 1203, 1096, 1045, 1014, 1000, 959, 894, 852, 814, 792, 755, 736, 700, 659 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.18 (3H, t, *J* = 7.2 Hz, CH₃), 3.03 (3H, s, CH₃), 3.36 (1H, dd, *J* = 2.1, 7.2 Hz, CH), 4.02–4.17 (2H, m, CH₂), 4.20–4.25 (1H, m, CH), 4.64 (1H, d, *J* = 1.2 Hz, CH), 6.98–6.99 (1H, m, CH), 7.40 (2H, d, *J* = 9.0 Hz, ArH), 8.21 (2H, d, *J* = 9.0 Hz, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.9, 25.2, 52.1, 52.7, 52.9, 61.2, 124.0, 128.0, 138.6, 140.4, 147.2, 149.1, 162.4, 174.8, 177.3; MS (ESI) *m/z* (%): 345.0 (100) [M⁺ + 1]; HRMS (ESI) Calcd. for C₁₇H₁₆N₂NaO₆ (M⁺ + Na) requires 367.0901, found: 367.0893; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 214 nm; eluent: hexane/isopropanol 50/50; Flow rate: 0.7 mL/min; *t*_{major} = 39.74 min, *t*_{minor} = 46.57 min; ee = 98%; [α]_D²⁰ = +282.8 (c 1.0, CHCl₃).



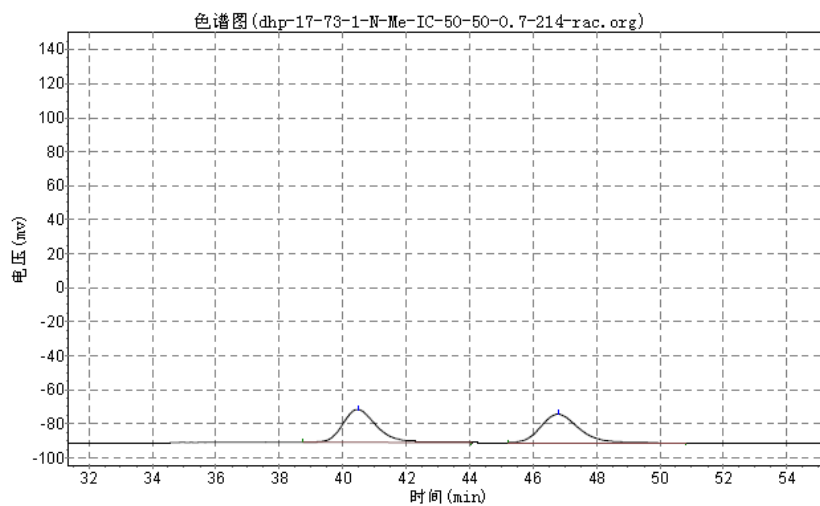
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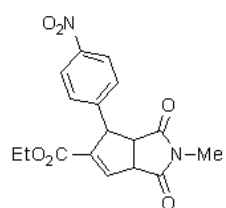
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积分方法: 面积归一法



分析结果表

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2		46.798	16573.801	1372712.250	49.2841
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rac

IC-H, 214 nm
Hexane:PrOH = 50:50
0.7 mL/min

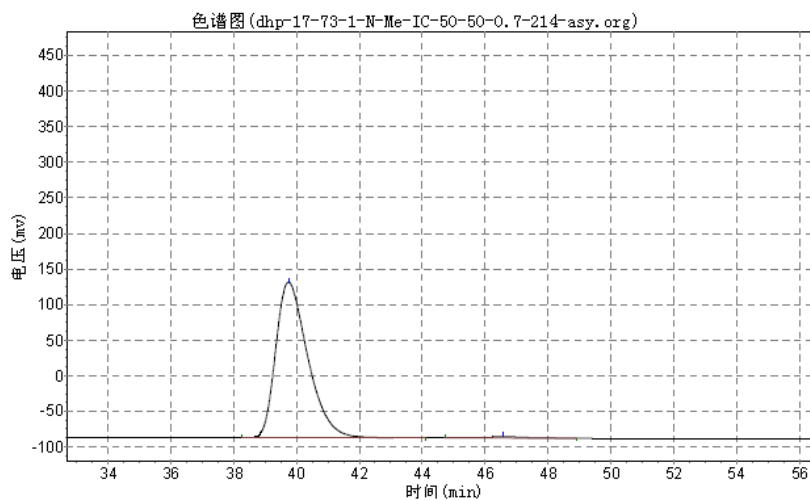
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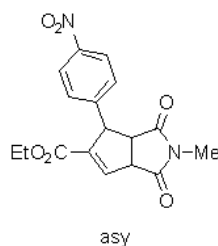
实验者:

报告时间: 2011-11-18, 21:48:57

积分方法: 面积归一法

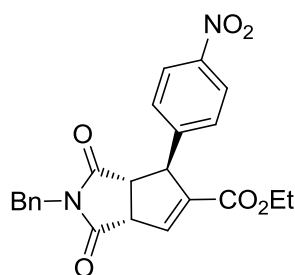


分析结果表					
峰号	峰名	保留时间	峰高	峰面积	含量
1		39.743	218998.922	15517876.000	99.0861
2		46.575	1748.814	143119.609	0.9139
总计			220747.736	15660995.609	100.0000



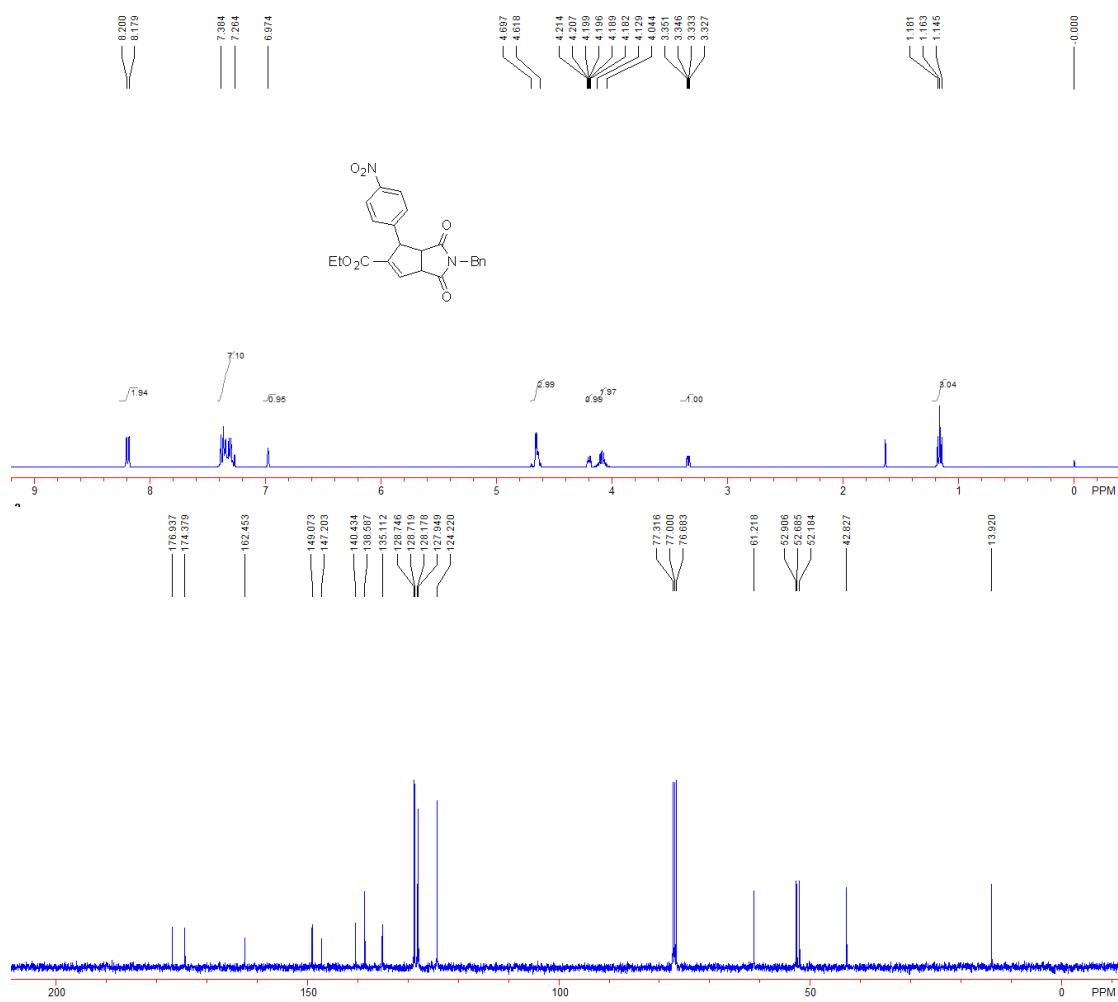
IC-H, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

Chiral HPLC Report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 39.74$ min, $t_{\text{minor}} = 46.57$ min; ee = 98%; $[\alpha]_{\text{D}}^{20} = +282.8$ (c 1.0, CHCl_3)].



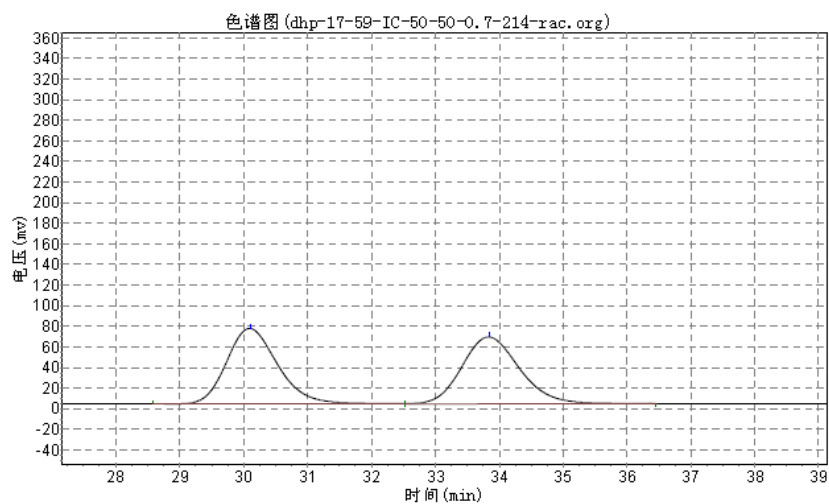
(3aR,4S,6aS)-ethyl 2-benzyl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3c). Yield: 36 mg, 86%; yellow oil; IR (CH_2Cl_2): ν 3077, 3033,

2981, 2936, 1776, 1708, 1635, 1604, 1558, 1455, 1431, 1393, 1348, 1271, 1202, 1169, 1095, 1054, 1014, 991, 931, 905, 851, 814, 753, 714, 699, 660 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.16 (3H, t, $J = 7.2$ Hz, CH_3), 3.34 (1H, dd, $J = 2.4, 7.2$ Hz, CH), 4.04–4.13 (2H, m, CH_2), 4.18–4.21 (1H, m, CH), 4.62–4.70 (3H, m, $\text{CH}_2 + \text{CH}$), 6.97 (1H, s, CH), 7.26–7.38 (7H, m, ArH), 8.18–8.20 (2H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 42.8, 52.2, 52.7, 52.9, 61.2, 124.2, 127.9, 128.2, 128.72, 128.75, 135.1, 138.6, 140.4, 147.2, 149.1, 162.4, 174.4, 176.9; MS (ESI) m/z (%): 421.1 (100) $[\text{M}^+ + 1]$; HRMS (ESI) Calcd. for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_6$ ($\text{M}^+ + \text{Na}$) requires 443.1214, found: 443.1198; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 29.77$ min, $t_{\text{minor}} = 33.60$ min; ee = 94%; $[\alpha]_{\text{D}}^{20} = +243.3$ (c 1.0, CHCl_3)].



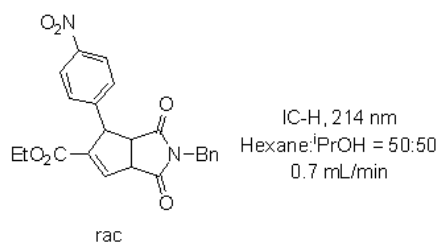
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实验者:
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积分方法: 面积归一法



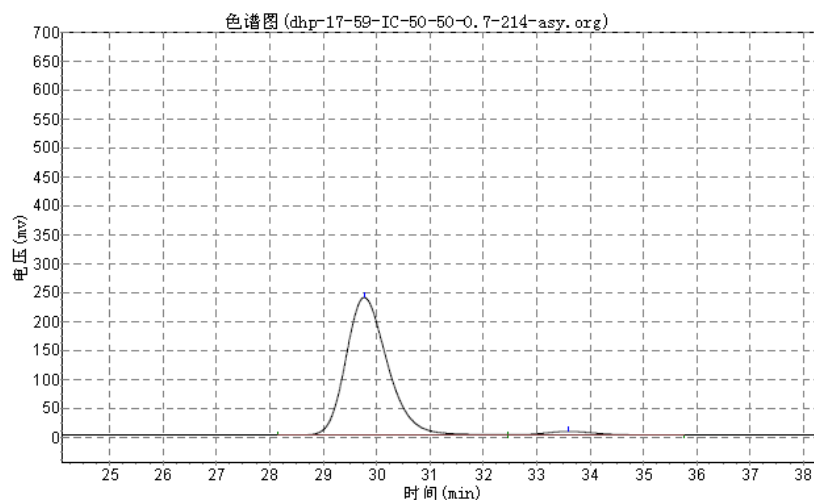
分析结果表

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2		33.857	64830.836	4063593.750	49.8905
总计			138116.383	8145032.750	100.0000

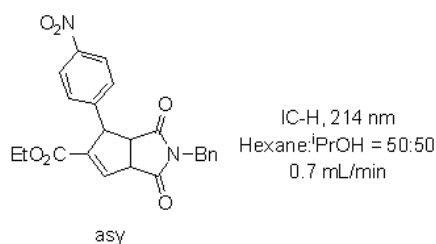


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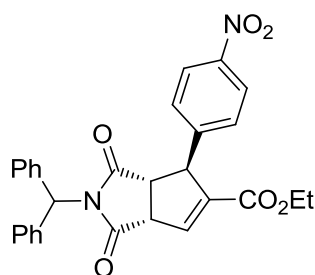
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积分方法: 面积归一法



分析结果表					
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1		29.773	237640.906	12853007.000	96.9194
2		33.605	6289.451	408535.344	3.0806
总计			243930.357	13261542.344	100.0000

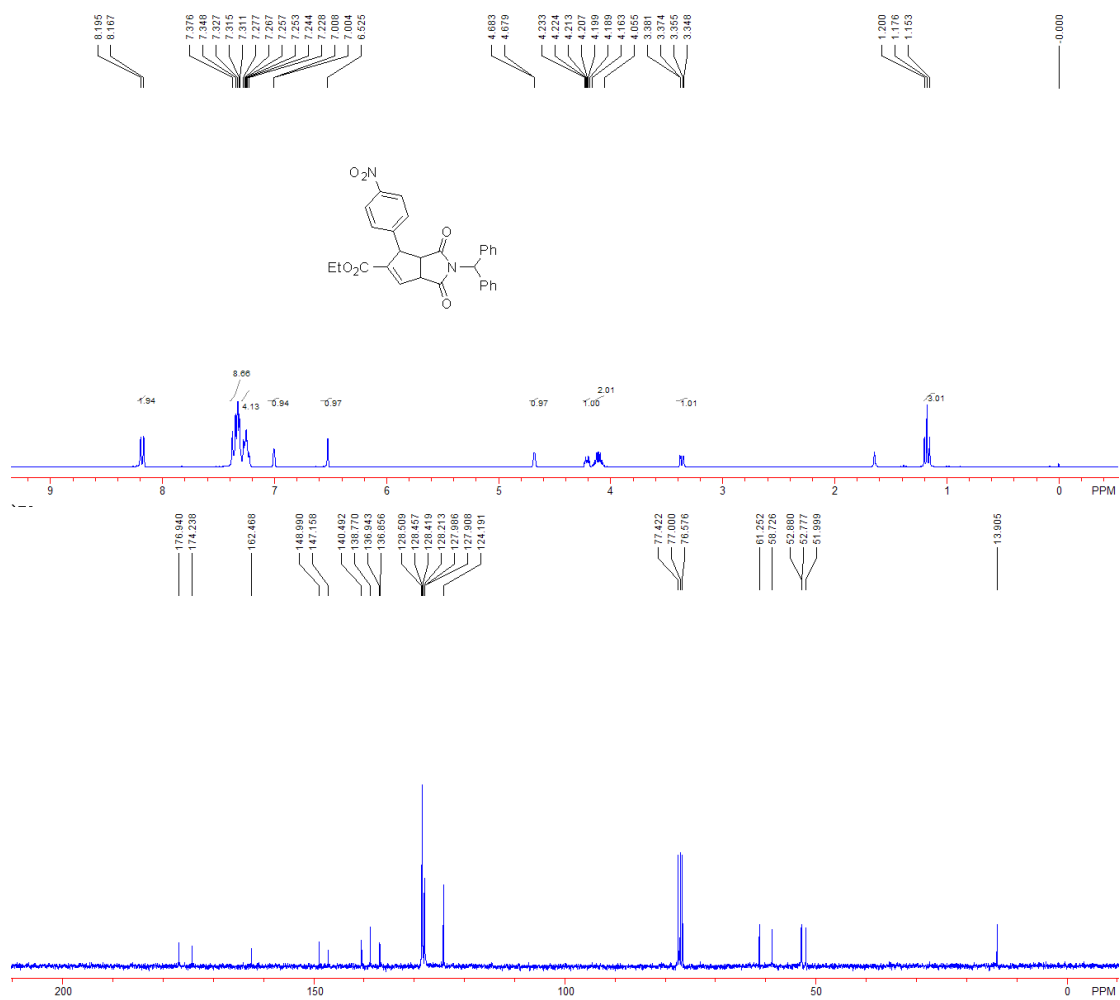


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 29.77$ min, $t_{\text{minor}} = 33.60$ min; ee = 94%; $[\alpha]_{\text{D}}^{20} = +243.3$ (c 1.0, CHCl_3)].



(3aR,4S,6aS)-ethyl 2-benzhydryl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3d). Yield: 50 mg, >99%; yellow oil; IR (CH_2Cl_2): ν 3064, 3030,

2924, 2853, 1776, 1712, 1634, 1598, 1520, 1495, 1449, 1348, 1272, 1190, 1170, 1094, 1031, 1014, 988, 920, 895, 853, 810, 738, 699, 663 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , TMS): δ 1.18 (3H, t, $J = 7.2$ Hz, CH_3), 3.36 (1H, dd, $J = 2.1, 7.8$ Hz, CH), 4.06–4.16 (2H, m, CH_2), 4.19–4.23 (1H, m, CH), 4.68 (1H, d, $J = 1.2$ Hz, CH), 6.52 (1H, s, CH), 7.00 (1H, d, $J = 1.2$ Hz, CH), 7.23–7.28 (4H, m, ArH), 7.31–7.38 (8H, m, ArH), 8.17–8.20 (2H, m, ArH); ^{13}C NMR (75 MHz, CDCl_3 , TMS): δ 13.9, 52.0, 52.8, 52.9, 58.7, 61.2, 124.2, 127.9, 128.0, 128.2, 128.42, 128.46, 128.5, 136.8, 136.9, 138.8, 140.5, 147.2, 149.0, 162.5, 174.2, 176.9; MS (ESI) m/z (%): 497.0 (100) $[\text{M}^+ + 1]$; HRMS (ESI) Calcd. for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{NaO}_6$ ($\text{M}^+ + \text{Na}$) requires 519.1527, found: 519.1507; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 16.59$ min, $t_{\text{minor}} = 21.27$ min; ee = 98%; $[\alpha]_{\text{D}}^{20} = +271.7$ (c 1.0, CHCl_3)].



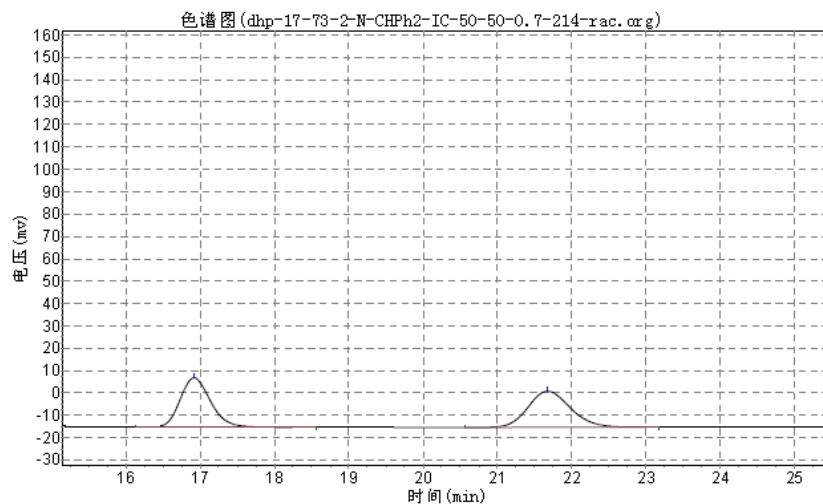
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实验者:

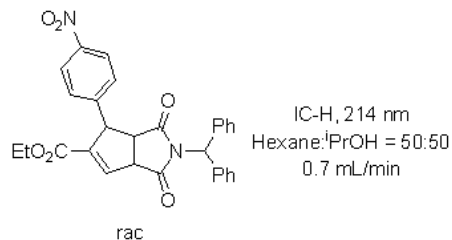
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积分方法: 面积归一法



分析结果表

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1		16.918	22167.262	637809.063	49.5466
2		21.677	16221.405	649481.438	50.4534
总计			38388.667	1287290.500	100.0000



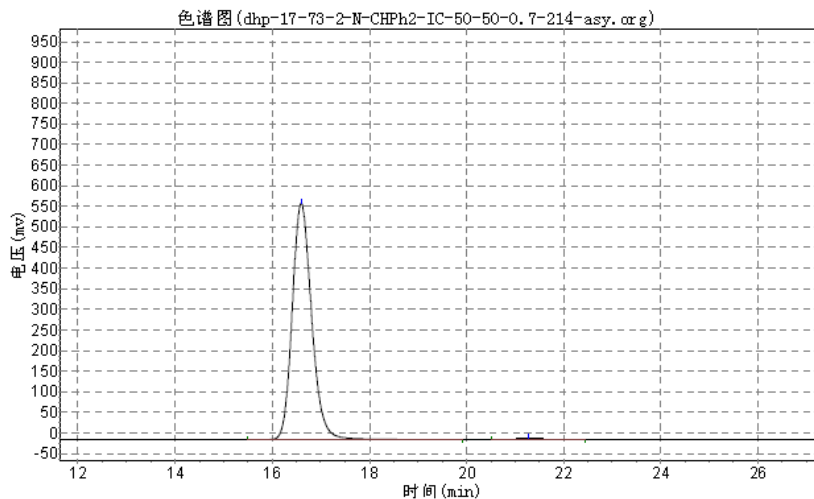
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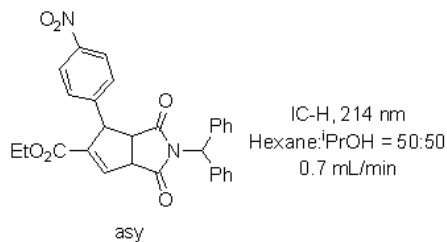
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积分方法: 面积归一法

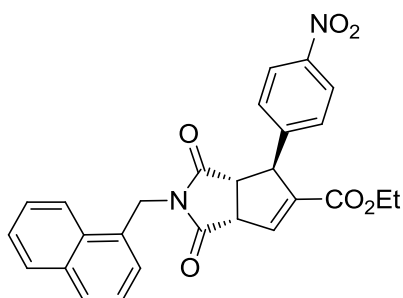


分析结果表

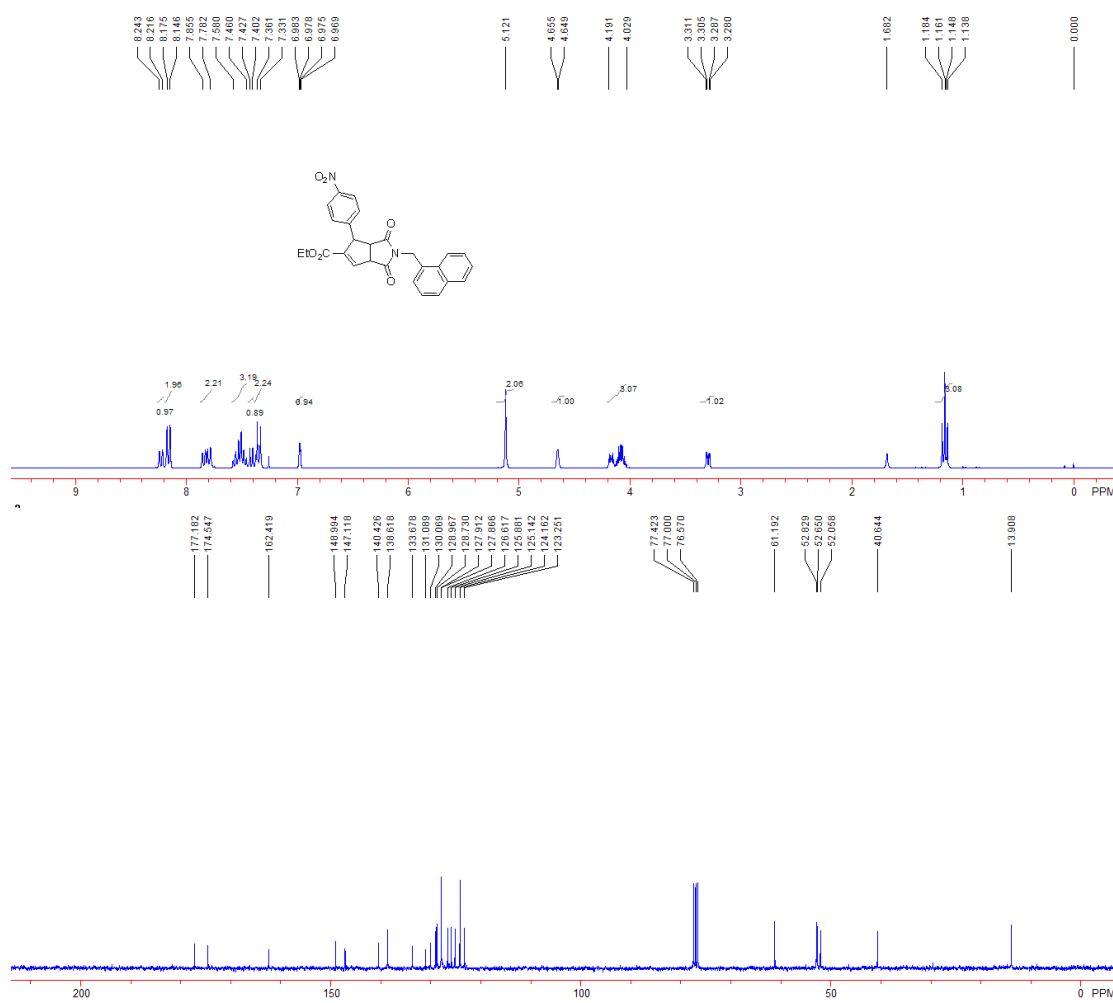
峰号	峰名	保留时间	峰高	峰面积	含量
1		16.593	573381.438	15920479.000	99.1817
2		21.275	3427.888	131353.188	0.8183
总计			576809.325	16051832.188	100.0000



Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 16.59$ min, $t_{\text{minor}} = 21.27$ min; ee = 98%; $[\alpha]_D^{20} = +271.7$ (c 1.0, CHCl₃)].

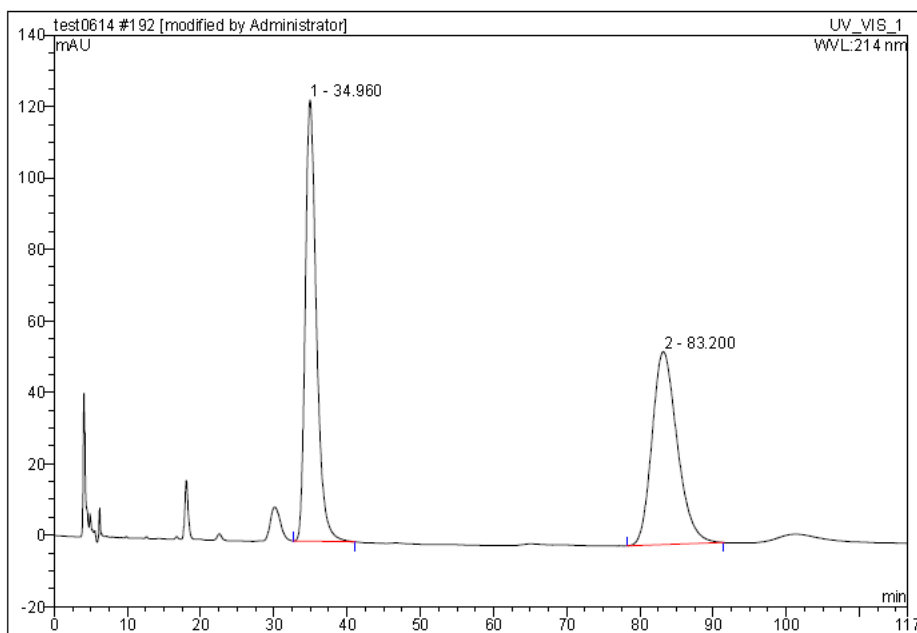


(3a*R*,4*S*,6a*S*)-ethyl 2-(naphthalen-1-ylmethyl)-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-5-carboxylate (3e). Yield: 43 mg, 91%; yellow oil; IR (CH₂Cl₂): ν 2981, 2920, 1777, 1708, 1635, 1598, 1519, 1428, 1394, 1347, 1271, 1174, 1096, 1014, 990, 852, 792, 778, 736, 699 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.16 (3H, t, *J* = 6.9 Hz, CH₃), 3.30 (1H, dd, *J* = 1.8, 7.2 Hz, CH), 4.03–4.19 (3H, m, CH+CH₂), 4.65 (1H, d, *J* = 1.8 Hz, CH), 5.12 (2H, s, CH₂), 6.98 (1H, dd, *J* = 1.8, 2.7 Hz, CH), 7.33–7.36 (2H, m, ArH), 7.42 (1H, d, *J* = 7.5 Hz, ArH), 7.46–7.58 (3H, m, ArH), 7.78–7.86 (2H, m, ArH), 8.16 (2H, d, *J* = 8.7 Hz, ArH), 8.23 (1H, d, *J* = 8.1 Hz, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.9, 40.6, 52.0, 52.6, 52.8, 61.2, 123.2, 124.2, 125.1, 125.9, 126.6, 127.9, 128.7, 129.0, 130.1, 131.1, 133.7, 138.6, 140.4, 147.1, 149.0, 162.4, 174.5, 177.2; MS (ESI) *m/z* (%): 471.0 (100) [M⁺ + 1]; HRMS (ESI) Calcd. for C₂₇H₂₂N₂NaO₆ (M⁺ + Na) requires 493.1370, found: 493.1363; Enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column [λ = 214 nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; *t*_{major} = 34.85 min, *t*_{minor} = 83.52 min; ee = 96%; [α]_D²⁰ = +204.5 (*c* 1.0, CHCl₃)].

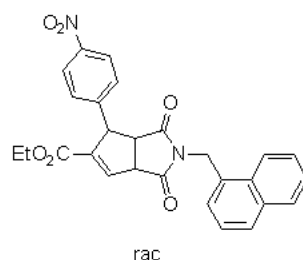


192 DHP-17-72-3+- PC-2 55 214 0.7

Sample Name:	DHP-17-72-3+- PC-2 55 214 0.7	Injection Volume:	5.0
Vial Number:	RA1	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2011-8-19 11:02	Sample Weight:	1.0000
Run Time (min):	116.57	Sample Amount:	1.0000



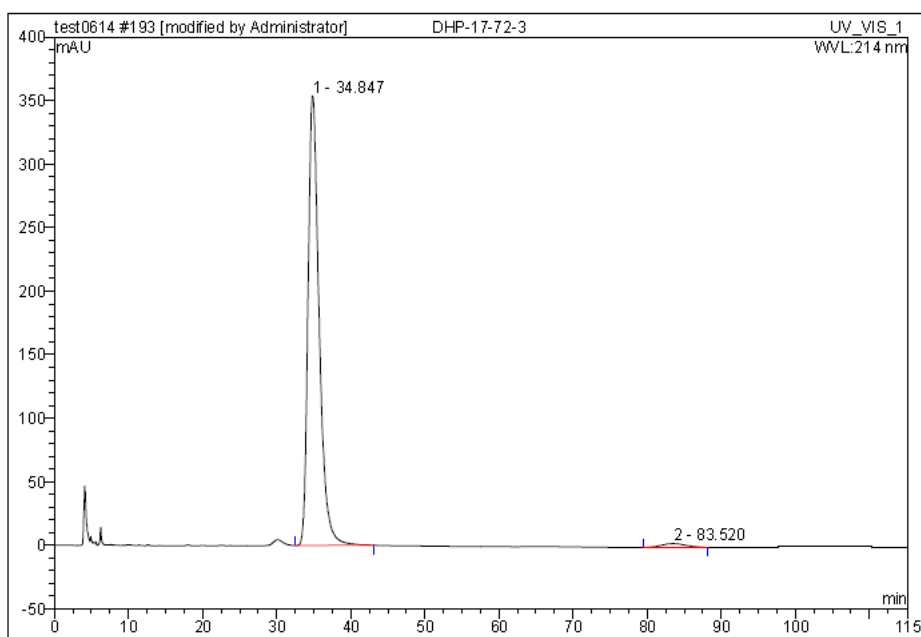
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	34.96	n.a.	123.529	217.480	50.18	n.a.	BMB
2	83.20	n.a.	54.025	215.933	49.82	n.a.	BMB
Total:			177.554	433.413	100.00	0.000	



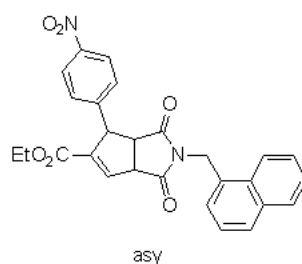
PC-2, 214 nm
Hexane:PrOH = 50:50
0.7 mL/min

193 DHP-17-72-3

Sample Name:	DHP-17-72-3	Injection Volume:	5.0
Vial Number:	RA2	Channel:	UV_VIS_1
Sample Type:	unknown	Wavelength:	214
Control Program:	WXL	Bandwidth:	n.a.
Quantif. Method:	WXL	Dilution Factor:	1.0000
Recording Time:	2011-8-19 13:00	Sample Weight:	1.0000
Run Time (min):	115.18	Sample Amount:	1.0000



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	34.85	n.a.	353.746	613.639	98.18	n.a.	BMB*
2	83.52	n.a.	3.027	11.382	1.82	n.a.	BMB*
Total:			356.773	625.022	100.00	0.000	

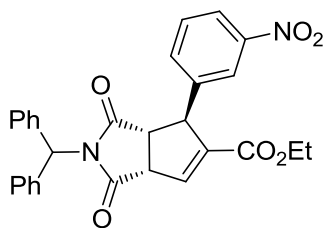


PC-2, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

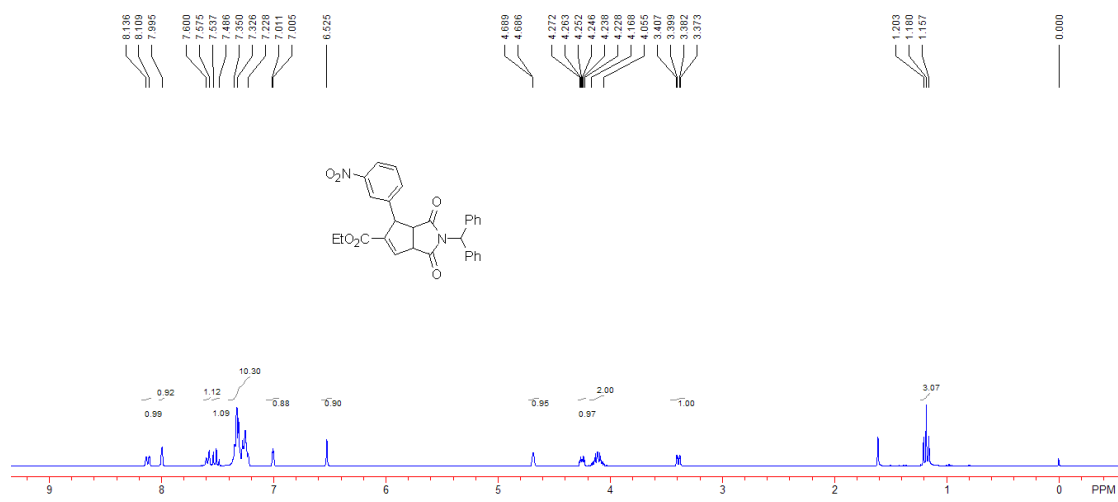
default/Integration

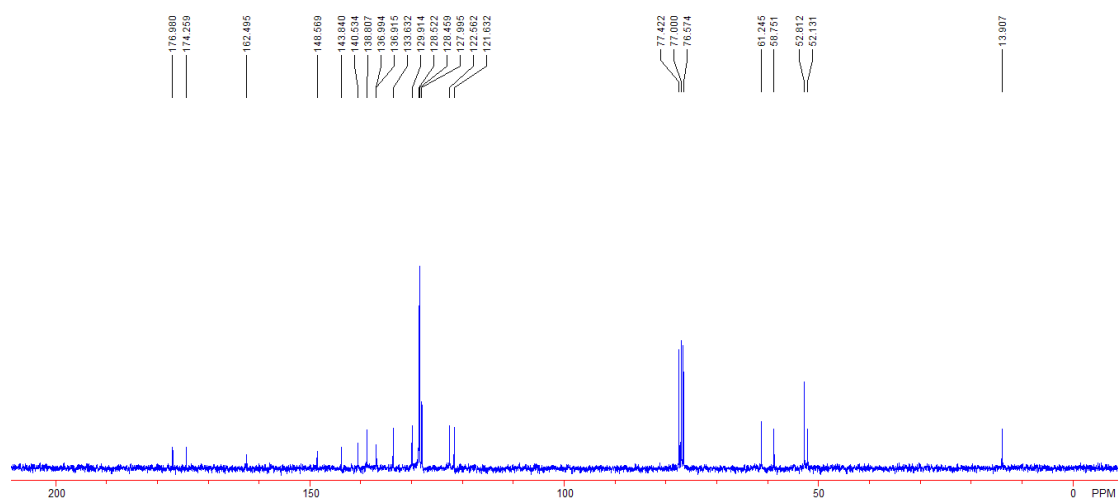
Chromeleon (c) Dionex 1996-2006
Version 6.80 SR10 Build 2818 (166959)

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column
[$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 34.85$ min, $t_{\text{minor}} = 83.52$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +204.5$ (c 1.0, CHCl_3)].



(3aR,4S,6aS)-ethyl 2-benzhydryl-4-(3-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3f). Yield: 43 mg, 87%; yellow oil; IR (CH₂Cl₂): ν 3064, 3030, 2981, 2931, 1777, 1712, 1633, 1600, 1584, 1530, 1496, 1477, 1449, 1352, 1271, 1190, 1171, 1095, 1031, 989, 892, 873, 858, 808, 737, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.18 (3H, t, J = 6.9 Hz, CH₃), 3.39 (1H, dd, J = 2.4, 7.5 Hz, CH), 4.06–4.17 (2H, m, CH₂), 4.23–4.27 (1H, m, CH), 4.69 (1H, d, J = 0.9 Hz, CH), 6.52 (1H, s, CH), 7.01 (1H, d, J = 0.9 Hz, CH), 7.23–7.35 (10H, m, ArH), 7.49–7.54 (1H, m, ArH), 7.59 (1H, d, J = 7.5 Hz, ArH), 8.00 (1H, s, ArH), 8.12 (1H, d, J = 8.1 Hz, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.9, 52.1, 52.8, 58.8, 61.2, 121.6, 122.6, 128.0, 128.4, 128.5, 129.9, 133.6, 136.9, 138.8, 140.5, 143.8, 148.6, 162.5, 174.2, 177.0; MS (ESI) m/z (%): 497.0 (100) [M⁺ + 1]; HRMS (ESI) Calcd. for C₂₉H₂₄N₂NaO₆ (M⁺ + Na) requires 519.1527, found: 519.1509; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 214 nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; t_{major} = 38.82 min, t_{minor} = 60.56 min; ee = 94%; $[\alpha]_{\text{D}}^{20}$ = +248.7 (c 1.0, CHCl₃)].



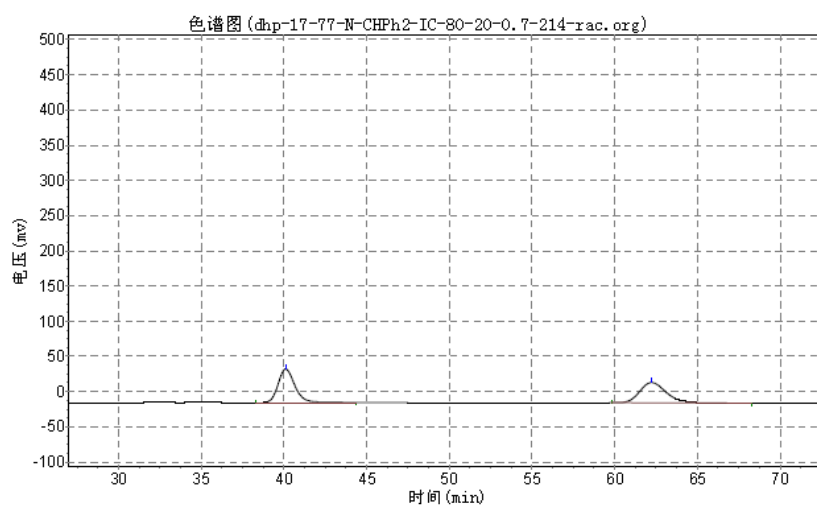


N2000 数据工作站

1

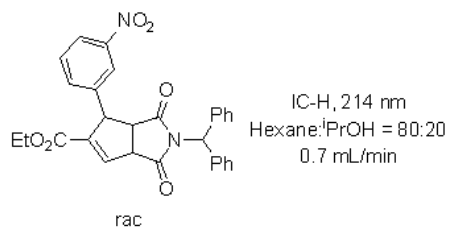
实验时间: 2011-08-22, 12:05:38
谱图文件: E:\实验数据\HPLC\dhp-17-77-N-CHPh2-IC-80-20-0.7-214-rac.org

实验者:
报告时间: 2011-11-18, 21:57:43
积分方法: 面积归一法



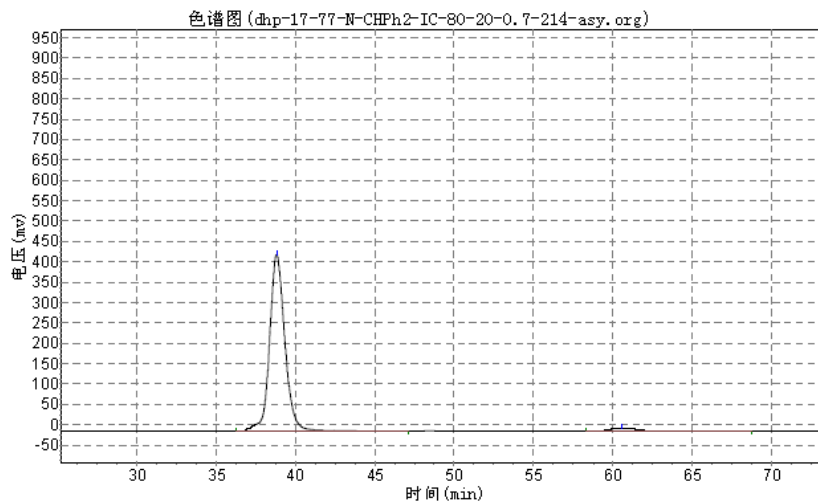
分析结果表

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2		62.227	28911.902	3235059.500	49.3914
总计			76429.805	6549838.500	100.0000



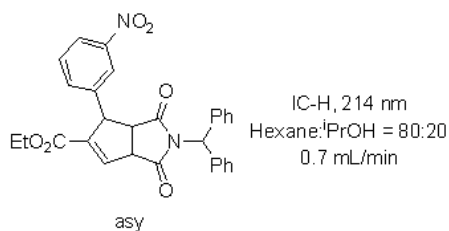
实验时间: 2011-08-22, 13:34:22
谱图文件: E:\实验数据\HPLC\dhp-17-77-N-CHPh2-IC-80-20-0.7-214-asy.org

实验者:
报告时间: 2011-11-18, 21:59:13
积分方法: 面积归一法

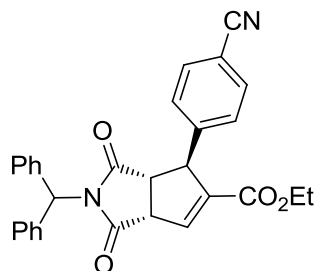


分析结果表

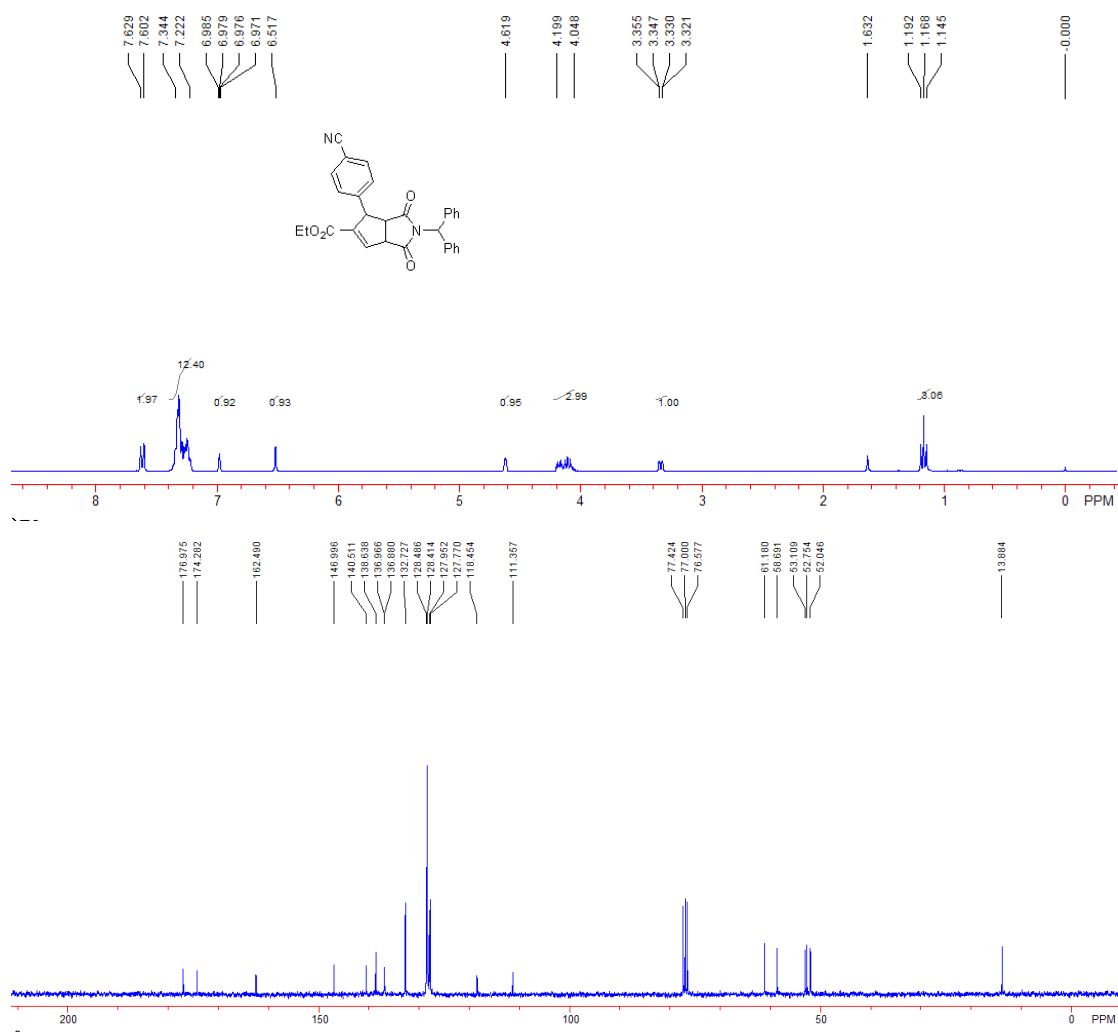
峰号	峰名	保留时间	峰高	峰面积	含量
1		38.817	432819.719	28980274.000	96.9618
2		60.562	7944.897	908075.500	3.0382
总计			440764.616	29888349.500	100.0000



Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 38.82$ min, $t_{\text{minor}} = 60.56$ min; ee = 94%; $[\alpha]_{\text{D}}^{20} = +248.7$ (c 1.0, CHCl_3)].

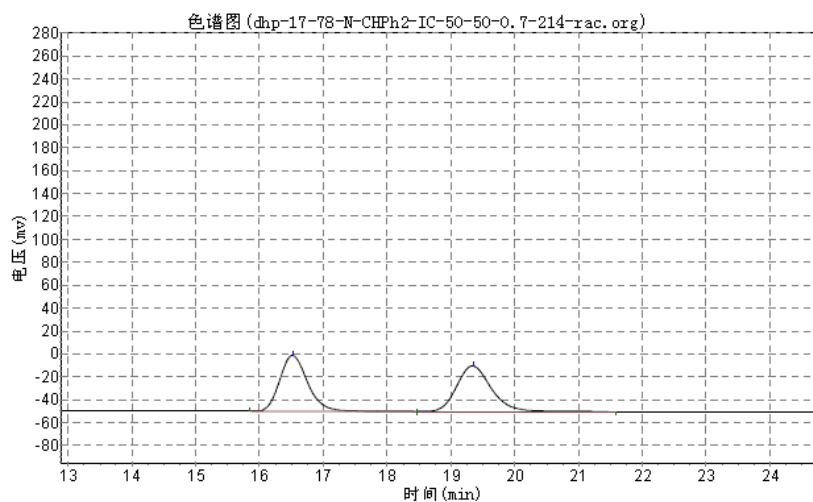


(3a*R*,4*S*,6a*S*)-ethyl 2-benzhydryl-4-(4-cyanophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-5-carboxylate (3g). Yield: 40 mg, 84%; colorless oil; IR (CH₂Cl₂): ν 3030, 2982, 2228, 1776, 1712, 1634, 1607, 1496, 1449, 1348, 1355, 1327, 1271, 1189, 1170, 1094, 1019, 987, 919, 843, 807, 739, 700 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.17 (3H, t, *J* = 7.2 Hz, CH₃), 3.34 (1H, dd, *J* = 2.4, 7.5 Hz, CH), 4.05–4.20 (3H, m, CH+CH₂), 4.62 (1H, s, CH), 6.52 (1H, s, CH), 6.98 (1H, d, *J* = 1.8, 2.7 Hz, CH), 7.22–7.34 (12H, m, ArH), 7.62 (2H, d, *J* = 8.1 Hz, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.9, 52.0, 52.8, 53.1, 58.7, 61.2, 114.4, 118.4, 127.8, 128.0, 128.4, 128.5, 132.7, 136.9, 137.0, 138.6, 140.5, 147.0, 162.4, 174.3, 177.0; MS (ESI) *m/z* (%): 477.0 (100) [*M*⁺+1]; HRMS (ESI) Calcd. for C₃₀H₂₄N₂NaO₄ (*M*⁺ + Na) requires 499.1628, found: 499.1611; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 214 nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; *t*_{major} = 16.50 min, *t*_{minor} = 19.33 min; ee = 96%; [α]_D²⁰ = +299.1 (*c* 1.0, CHCl₃)].



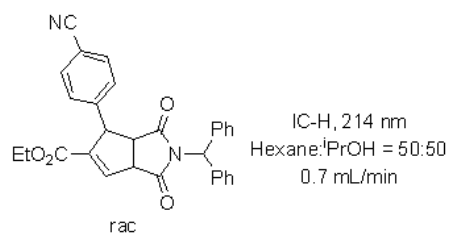
实验时间: 2011-08-21, 19:13:36
谱图文件: E:\实验数据\HPLC\dhp\17-78-N-CHPh2-IC-50-50-0.7-214-rac.org

实验者:
报告时间: 2011-11-18, 21:59:42
积分方法: 面积归一法



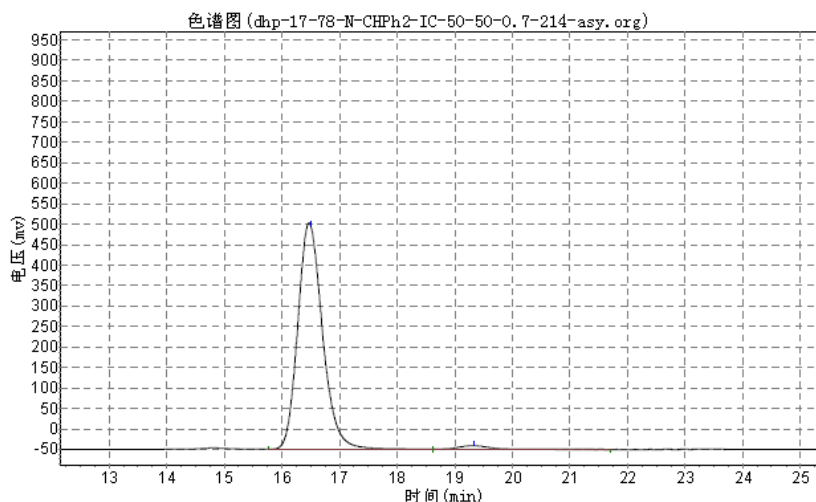
分析结果表

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2		19.357	39720.594	1494810.125	49.9867
总计			88556.848	2990415.125	100.0000



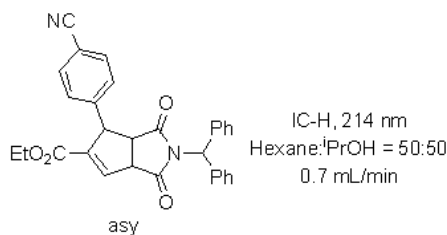
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实验者:
报告时间: 2011-11-18, 22:00:34
积分方法: 面积归一法

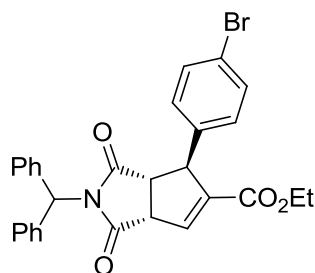


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.498	550996.250	16559629.000	97.8055
2		19.332	9099.071	371545.938	2.1944
总计			560095.321	16931174.938	100.0000

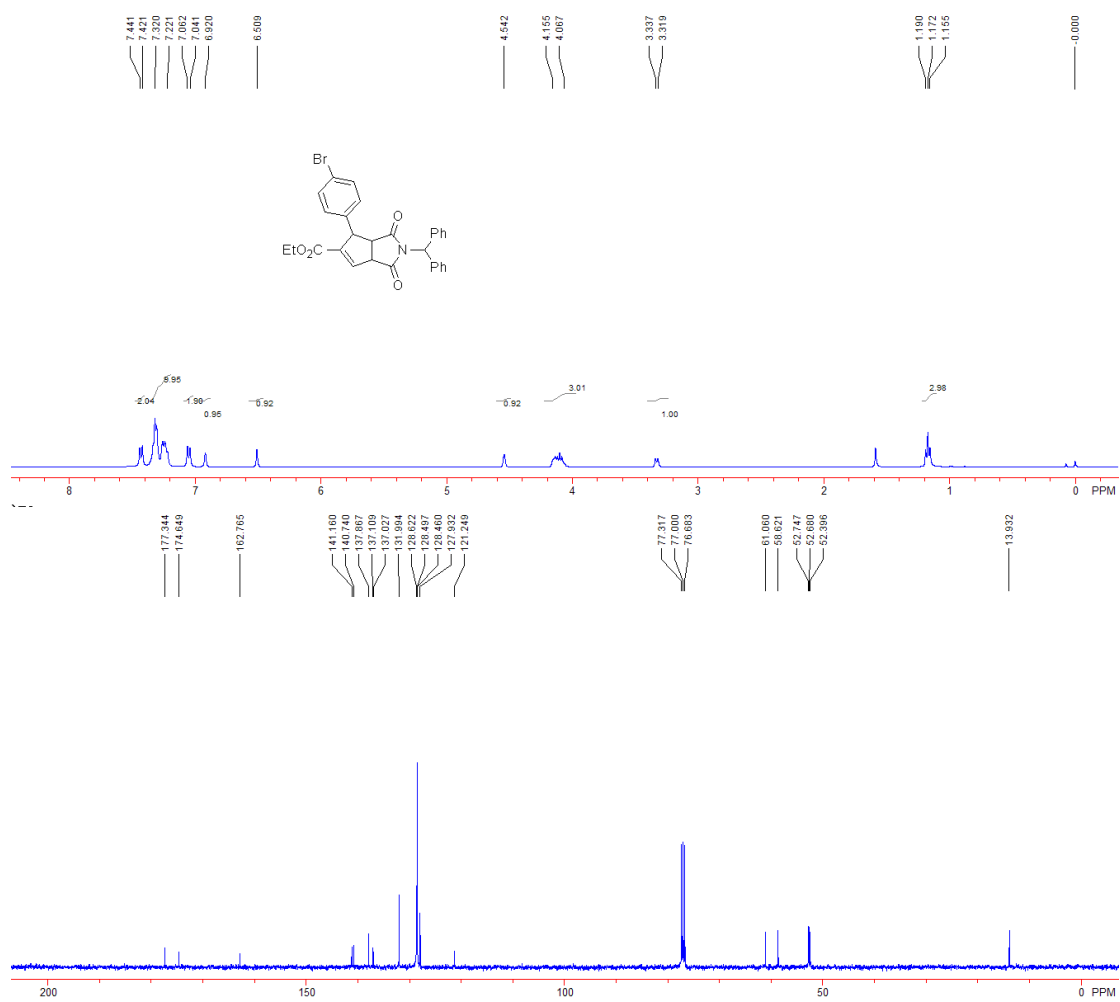


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 16.50$ min, $t_{\text{minor}} = 19.33$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +299.1$ (c 1.0, CHCl_3)].



(3aR,4S,6aS)-ethyl 2-benzhydryl-4-(4-bromophenyl)-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3h). Yield: 39 mg, 74%; colorless oil; IR (CH_2Cl_2): ν 3029, 2980,

1775, 1712, 1635, 1488, 1448, 1383, 1354, 1270, 1190, 1170, 1093, 1011, 987, 918, 877, 734, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 3.33 (1H, d, $J = 7.2$ Hz, CH), 4.07–4.16 (3H, m, $\text{CH} + \text{CH}_2$), 4.54 (1H, s, CH), 6.51 (1H, s, CH), 6.92 (1H, s, CH), 7.05 (2H, d, $J = 8.4$ Hz, ArH), 7.22–7.32 (10H, m, ArH), 7.43 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 52.4, 52.68, 52.75, 58.6, 61.1, 121.2, 127.9, 128.46, 128.49, 128.6, 132.0, 137.0, 137.9, 140.7, 141.2, 162.8, 174.6, 177.3; MS (ESI) m/z (%): 530.0 (100) [$\text{M}^+ + 1$]; HRMS (MALDI) Calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_4\text{BrNa}$ ($\text{M}^+ + \text{Na}$) requires 552.0781, found: 552.0798; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 9.06$ min, $t_{\text{minor}} = 10.38$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +240.9$ (c 1.0, CHCl_3)].



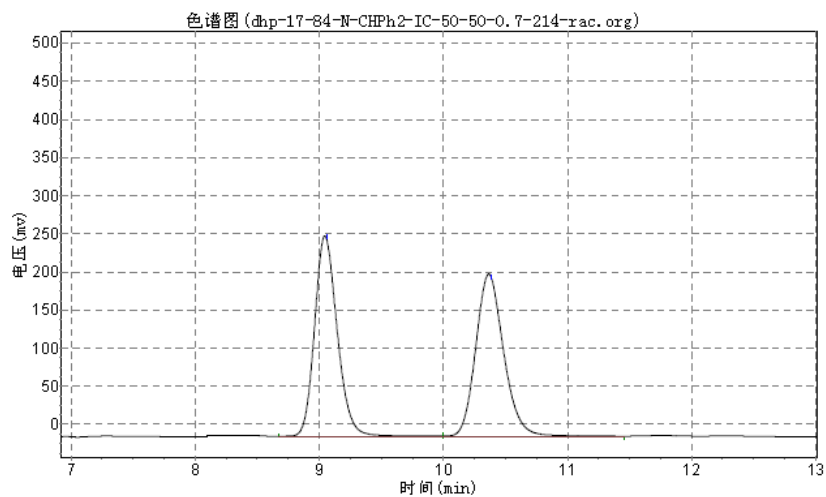
实验时间: 2011-08-29, 15:22:55

谱图文件: E:\实验数据\HPLC\dhp-17-84-N-CHPh2-IC-50-50-0.7-214-rac.org

实验者:

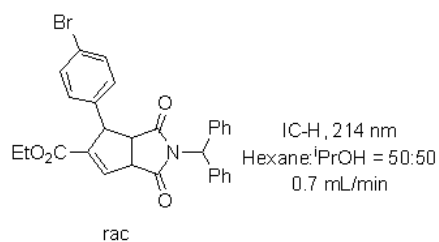
报告时间: 2011-11-18, 22:01:14

积分方法: 面积归一法



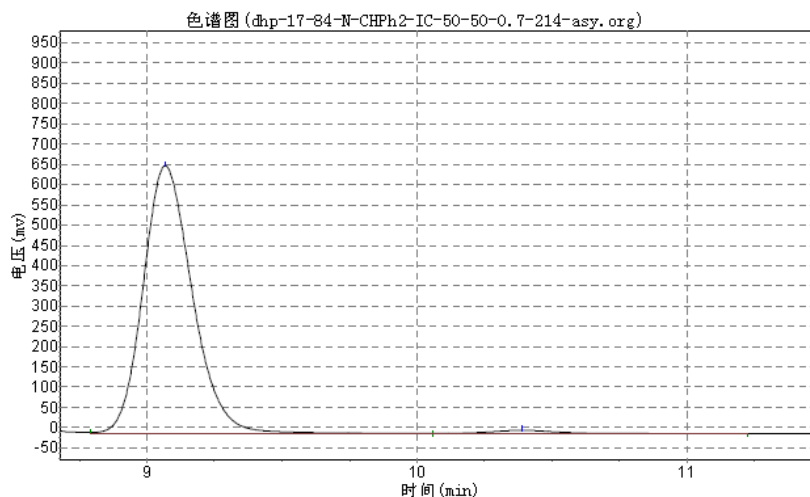
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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2		10.390	210492.000	3326024.250	49.9527
总计			471648.891	6658353.000	100.0000



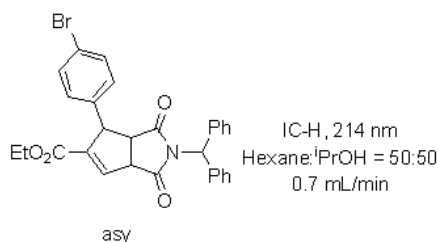
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实验者:
报告时间: 2011-11-18, 22:02:33
积分方法: 面积归一法

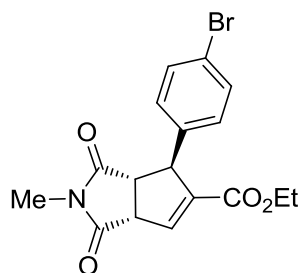


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.067	661049.063	8379444.000	98.4997
2		10.388	7945.128	127628.711	1.5003
总计			668994.191	8507072.711	100.0000

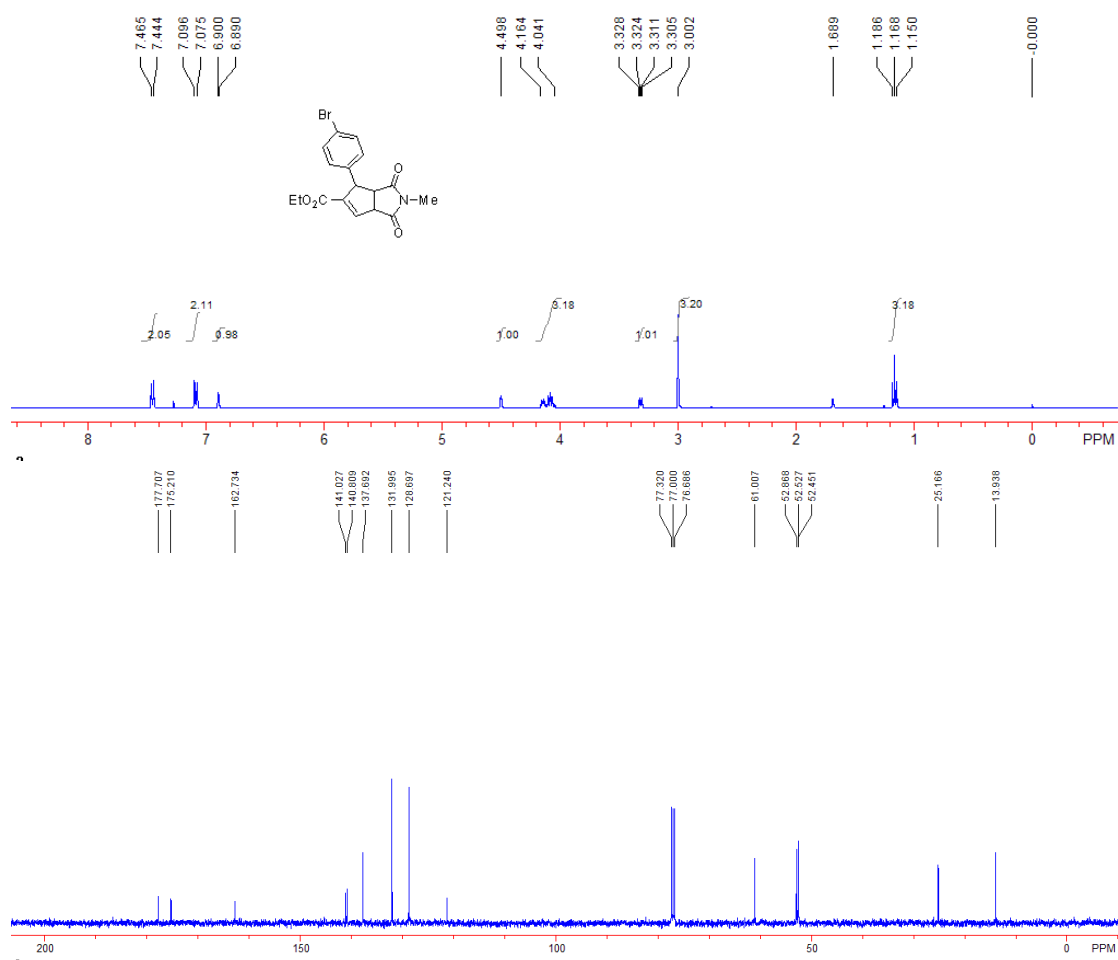


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 9.06$ min, $t_{\text{minor}} = 10.38$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +240.9$ (c 1.0, CHCl_3)].



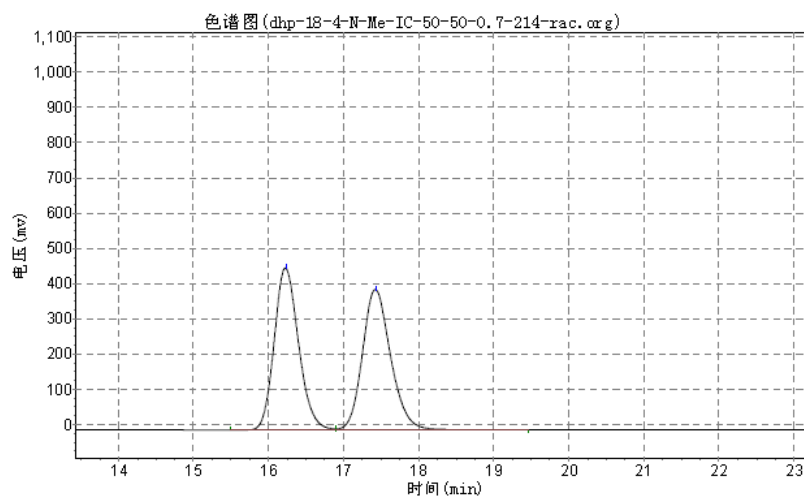
(3aR,4S,6aS)-ethyl 4-(4-bromophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (**3i**). Yield: 30 mg, 79%; colorless oil; IR (CH_2Cl_2): ν 2981, 1781,

1714, 1653, 1634, 1558, 1540, 1521, 1506, 1488, 1433, 1409, 1378, 1327, 1272, 1202, 1127, 1095, 1071, 1011, 960, 891, 874, 828, 790, 740, 715 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 3.00 (3H, s, CH_3), 3.32 (1H, dd, $J = 1.6, 6.8$ Hz, CH), 4.04–4.16 (3H, m, CH+ CH_2), 4.50 (1H, s, CH), 6.89–6.90 (1H, m, CH), 7.08–7.10 (2H, m, ArH), 7.44–7.46 (2H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 25.2, 52.4, 52.5, 52.9, 61.0, 121.2, 128.7, 132.0, 137.7, 140.8, 141.0, 162.7, 175.2, 177.7; MS (ESI) m/z (%): 378.0 (100) [$\text{M}^+ + 1$]; HRMS (MALDI) Calcd. for $\text{C}_{17}\text{H}_{16}\text{NO}_4\text{BrNa}$ ($\text{M}^+ + \text{Na}$) requires 400.0155, found: 400.0141; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 16.24$ min, $t_{\text{minor}} = 17.48$ min; ee = 95%; $[\alpha]_{\text{D}}^{20} = +239.9$ (c 1.0, CHCl_3)].



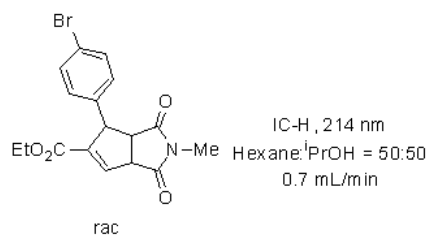
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实验者:
报告时间: 2011-11-18, 22:15:21
积分方法: 面积归一法



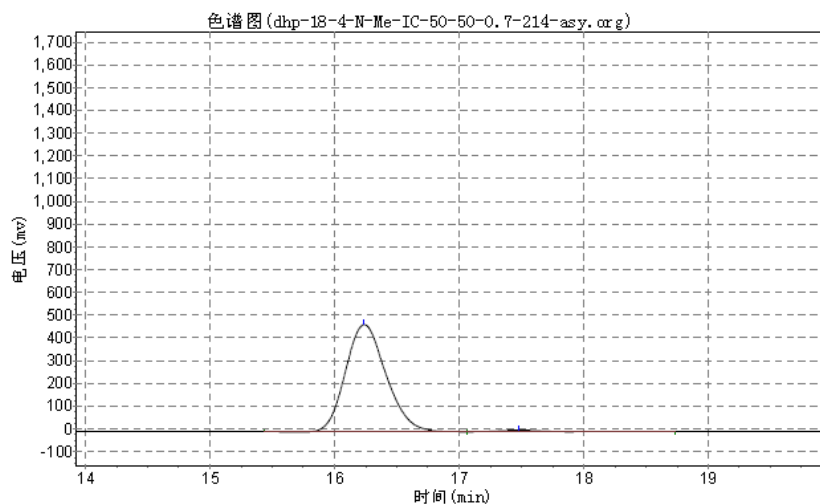
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.232	459044.594	10378357.000	49.9012
2		17.432	398001.969	10419444.000	50.0988
总计			857046.563	20797801.000	100.0000



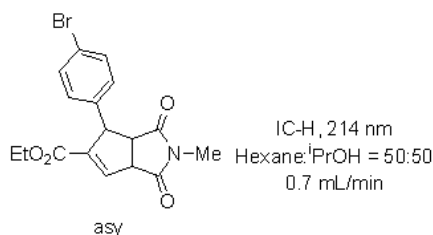
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实验者:
报告时间: 2011-11-18, 22:16:28
积分方法: 面积归一法

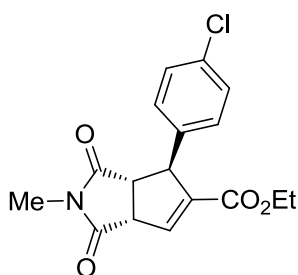


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.238	472927.594	10805376.000	97.4862
2		17.477	9626.848	278624.625	2.5138
总计			482554.441	11084000.625	100.0000

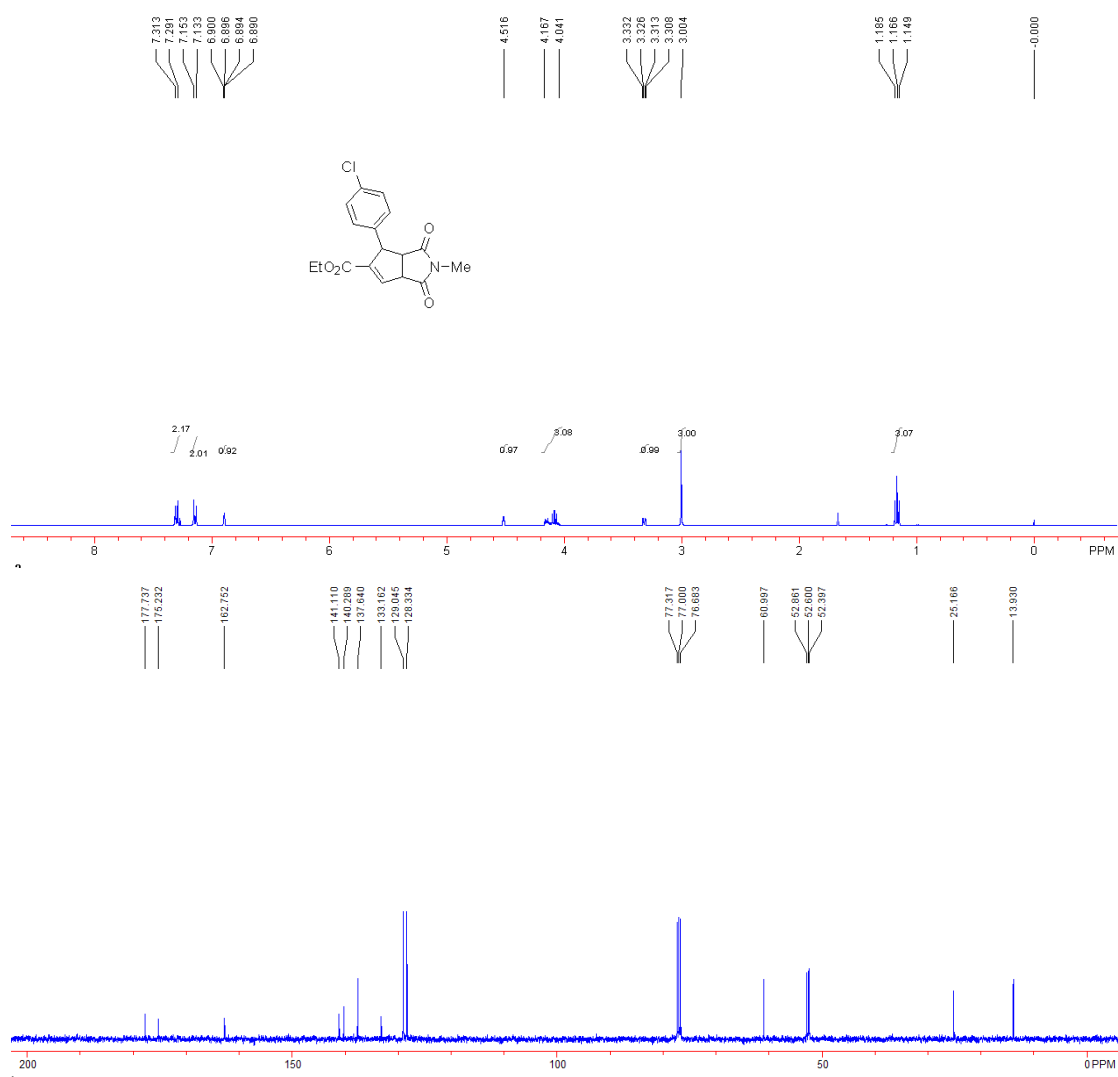


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 16.24$ min, $t_{\text{minor}} = 17.48$ min; ee = 95%; $[\alpha]_{\text{D}}^{20} = +239.9$ (c 1.0, CHCl_3)].



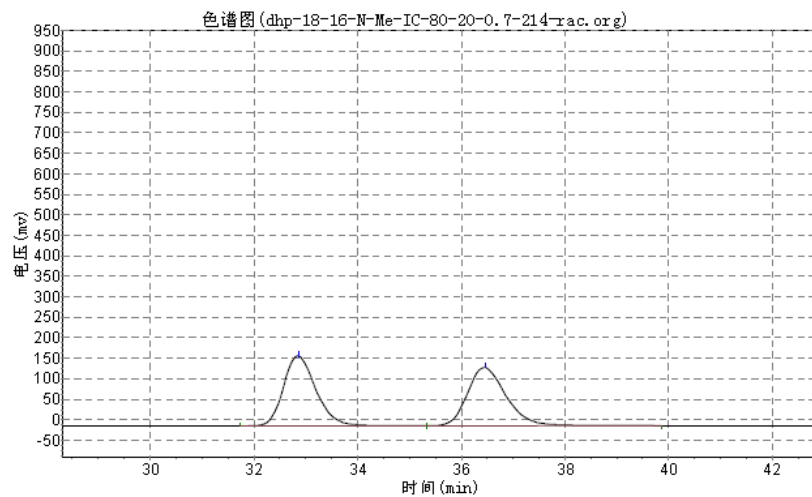
(3aR,4S,6aS)-ethyl 4-(4-chlorophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (**3j**). Yield: 30 mg, 90%; colorless oil; IR (CH_2Cl_2): ν 2982, 1781,

1704, 1634, 1491, 1434, 1379, 1272, 1202, 1127, 1093, 1045, 1014, 1001, 959, 891, 874, 790, 751, 739, 666 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.17 (3H, t, $J = 6.8$ Hz, CH_3), 3.00 (3H, s, CH_3), 3.32 (1H, dd, $J = 2.4, 7.6$ Hz, CH), 4.04–4.17 (3H, m, $\text{CH}+\text{CH}_2$), 4.52 (1H, s, CH), 6.90 (1H, dd, $J = 1.6, 2.4$ Hz, CH), 7.14 (2H, d, $J = 8.0$ Hz, ArH), 7.30 (2H, d, $J = 8.0$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 25.2, 52.4, 52.6, 52.9, 61.0, 128.3, 129.0, 133.2, 137.6, 140.3, 141.1, 162.8, 175.2, 177.7; MS (ESI) m/z (%): 334.0 (100) $[\text{M}^+ + 1]$; HRMS (MALDI) Calcd. for $\text{C}_{17}\text{H}_{16}\text{NO}_4\text{ClNa}$ ($\text{M}^+ + \text{Na}$) requires 356.0660, found: 356.0659; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 31.48$ min, $t_{\text{minor}} = 35.18$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +263.0$ (c 1.0, CHCl_3)].



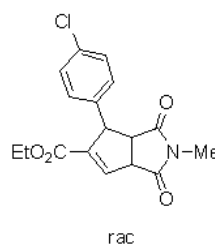
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实验者:
报告时间: 2011-11-18, 22:07:53
积分方法: 面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		32.865	169878.000	7370794.000	50.1006
2		36.465	141510.000	7341192.500	49.8994
总计			311388.000	14711986.500	100.0000



IC-H, 214 nm
Hexane: iPrOH = 80:20
0.7 mL/min

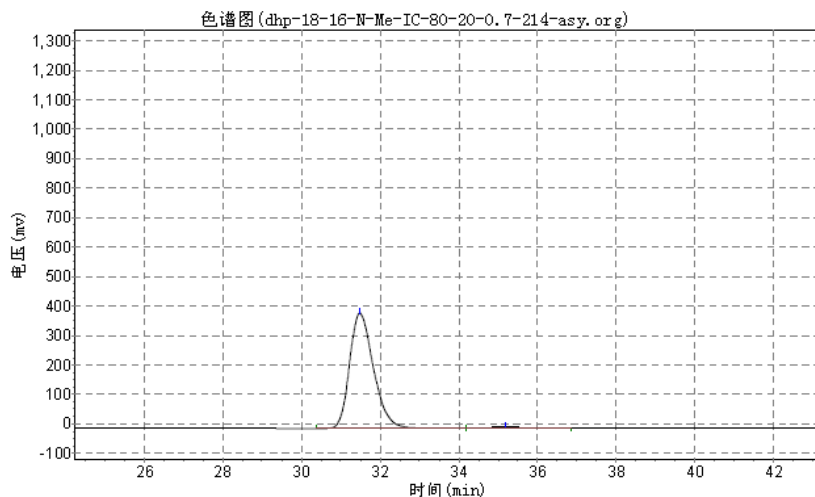
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实验者:

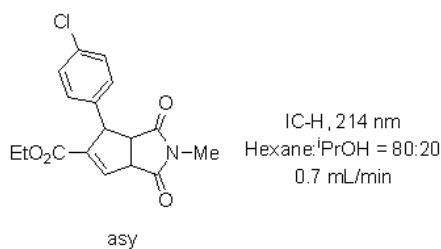
报告时间: 2011-11-18, 22:09:22

积分方法: 面积归一法

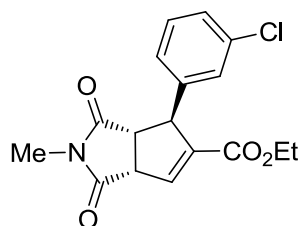


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		31.480	391102.375	16476227.000	98.2510
2		35.177	5563.332	293290.656	1.7490
总计			396665.707	16769517.656	100.0000

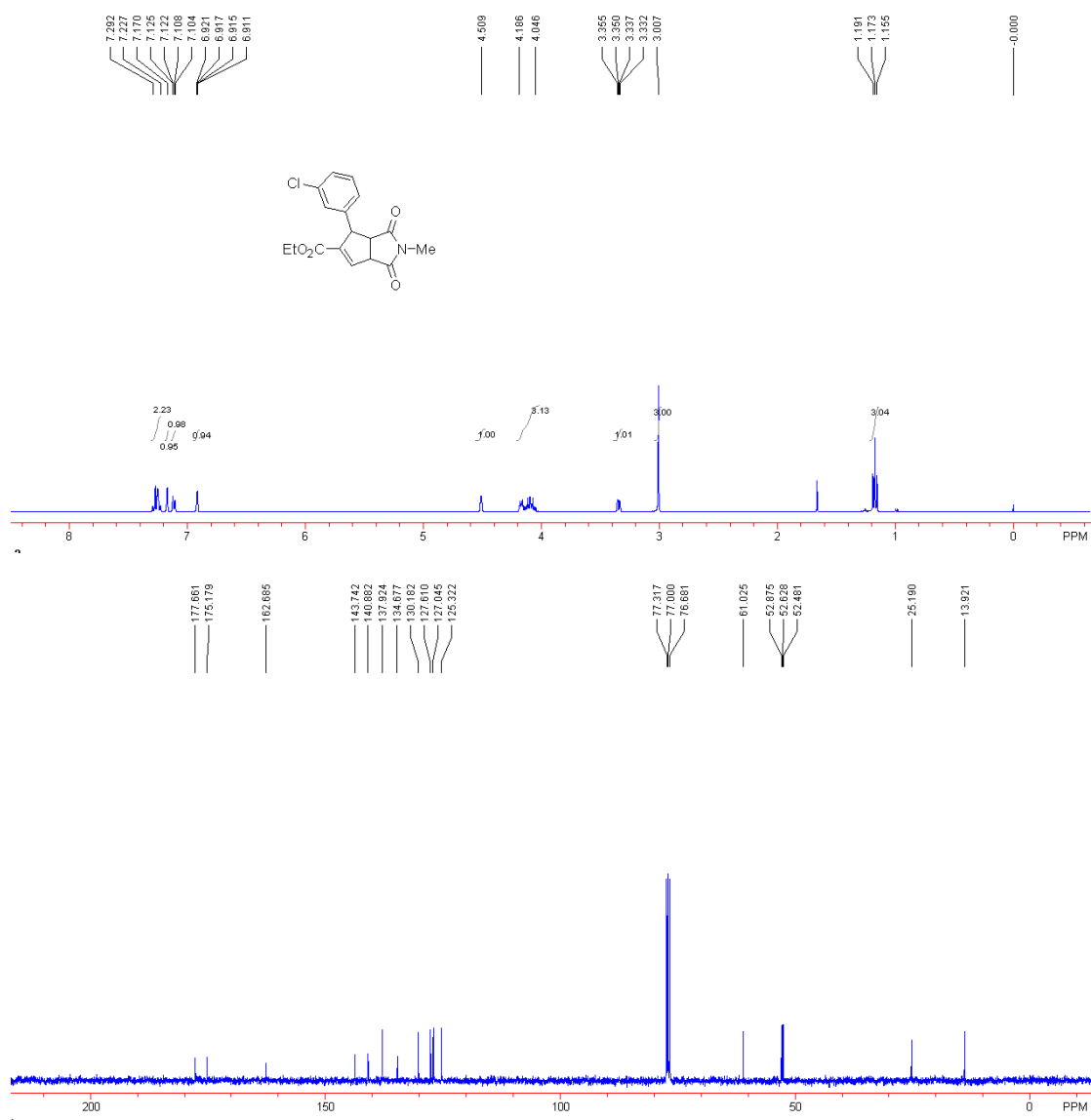


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 31.48$ min, $t_{\text{minor}} = 35.18$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +263.0$ (c 1.0, CHCl_3)].



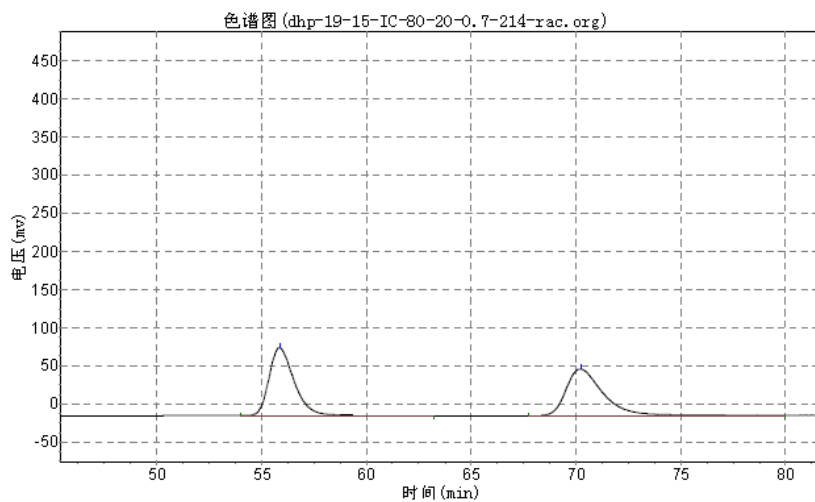
(3aR,4S,6aS)-ethyl 4-(3-chlorophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (**3k**). Yield: 27 mg, 81%; colorless oil; IR (CH_2Cl_2): ν 2981, 2936,

1699, 1595, 1432, 1378, 1270, 1203, 1127, 1095, 1001, 960, 783, 765, 737, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.17 (3H, t, $J = 7.2$ Hz, CH_3), 3.01 (3H, s, CH_3), 3.34 (1H, dd, $J = 2.0, 7.2$ Hz, CH), 4.05–4.19 (3H, m, CH+ CH_2), 4.51 (1H, s, CH), 6.92 (1H, dd, $J = 1.6, 2.4$ Hz, CH), 7.12 (1H, dd, $J = 1.6, 7.2$ Hz, ArH), 7.17 (1H, s, ArH), 7.23–7.29 (2H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 25.2, 52.5, 52.6, 52.9, 61.0, 125.3, 127.0, 127.6, 130.2, 134.7, 137.9, 140.9, 143.7, 162.7, 175.2, 177.7; MS (MALDI) m/z (%): 379.2 (100) [$\text{M}^+ + \text{HCO}_2\text{H}$]; HRMS (MALDI) Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_4\text{Cl}$ ($\text{M}^+ + 1$) requires 334.0841, found: 334.0847; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 55.36$ min, $t_{\text{minor}} = 70.69$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +316.0$ (c 1.0, CHCl_3)].



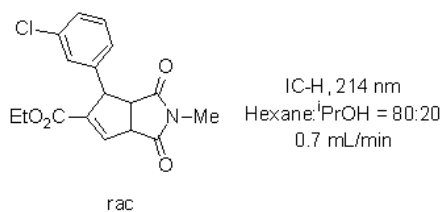
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rac.org

实验者:
报告时间: 2011-11-26, 10:41:37
积分方法: 面积归一法



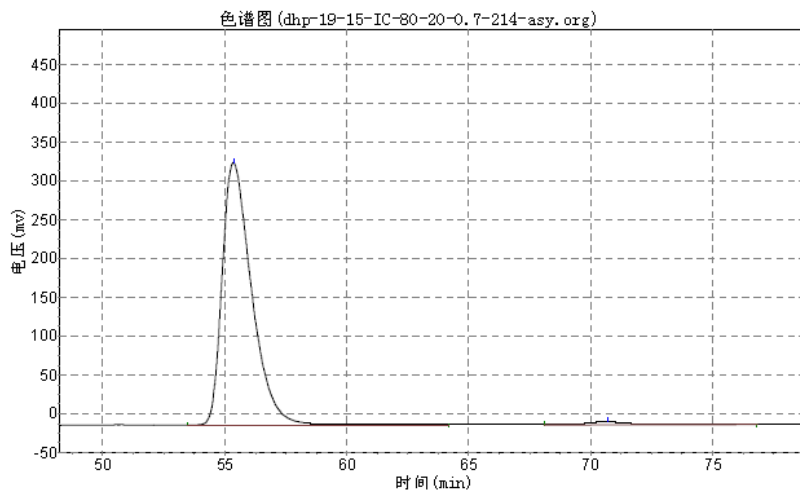
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		55.865	88220.570	7376706.500	50.1241
2		70.265	60781.105	7340167.500	49.8759
总计			149001.676	14716874.000	100.0000



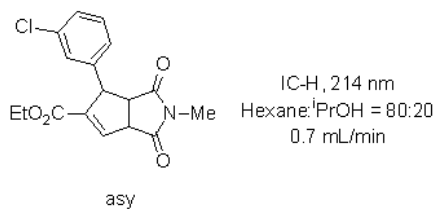
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实验者:
报告时间: 2011-11-26, 10:43:32
积分方法: 面积归一法

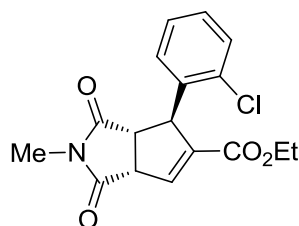


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		55.365	337659.688	28361346.000	98.3254
2		70.698	3539.049	483030.406	1.6746
总计			341198.737	28844376.406	100.0000

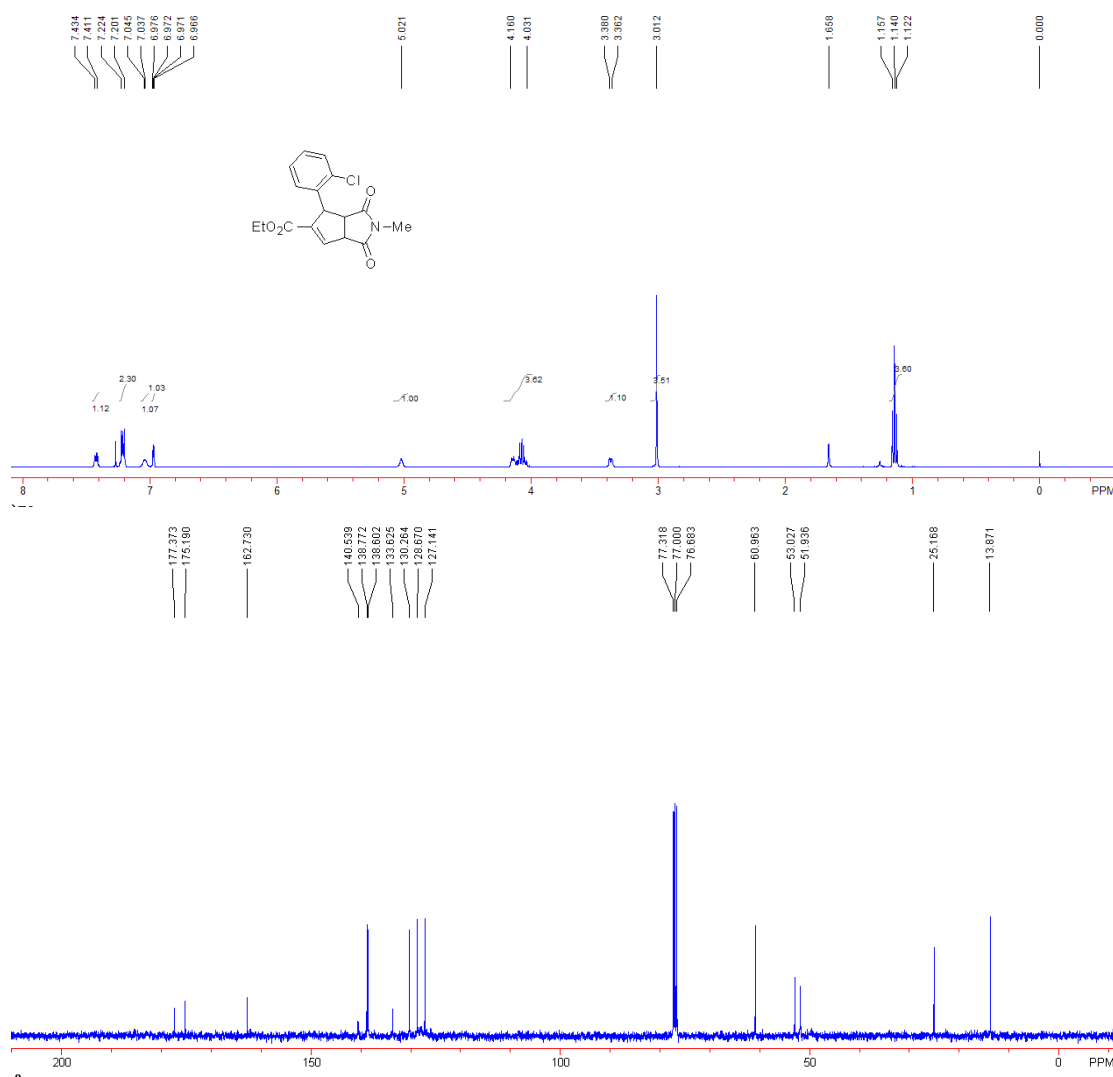


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 55.36$ min, $t_{\text{minor}} = 70.69$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +316.0$ (c 1.0, CHCl_3)].



(3aR,4R,6aS)-ethyl 4-(2-chlorophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (**3l**). Yield: 13 mg, 39%; colorless oil; IR (CH_2Cl_2): ν 2982, 1782,

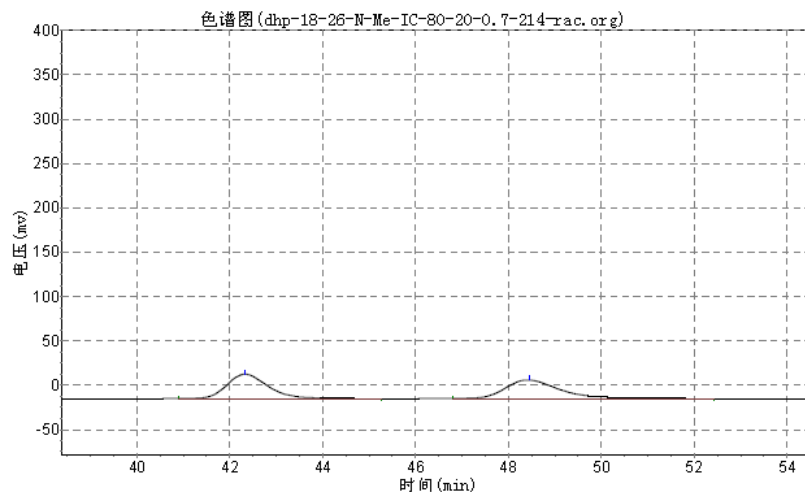
1705, 1635, 1474, 1433, 1378, 1307, 1268, 1201, 1127, 1096, 1052, 1037, 1000, 959, 792, 758, 690 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.14 (3H, t, $J = 7.2$ Hz, CH_3), 3.01 (3H, s, CH_3), 3.37 (1H, d, $J = 7.2$ Hz, CH), 4.03–4.16 (3H, m, CH+ CH_2), 5.02 (1H, s, CH), 6.97 (1H, dd, $J = 1.6, 2.0$ Hz, CH), 7.04–7.05 (1H, m, ArH), 7.20–7.22 (2H, m, ArH), 7.41–7.43 (1H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 25.2, 51.9, 53.2, 61.0, 127.1, 128.7, 130.3, 133.6, 138.6, 138.8, 140.5, 162.7, 175.2, 177.4; MS (ESI) m/z (%): 334.1 (100) [$\text{M}^+ + 1$]; HRMS (MALDI) Calcd. for $\text{C}_{17}\text{H}_{16}\text{NO}_4\text{ClNa}$ ($\text{M}^+ + \text{Na}$) requires 356.0660, found: 356.0651; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 42.76$ min, $t_{\text{minor}} = 48.89$ min; ee = 73%; $[\alpha]_{\text{D}}^{20} = +245.6$ (c 1.0, CHCl_3)].



实验时间: 2011-09-19, 18:08:24

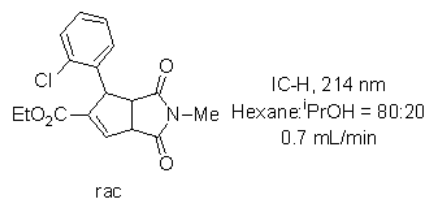
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实验者:

报告时间: 2011-11-18, 22:17:07
积分方法: 面积归一法

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		42.332	27284.703	1654170.375	50.1206
2		48.448	20712.541	1646209.250	49.8794
总计			47997.244	3300379.625	100.0000



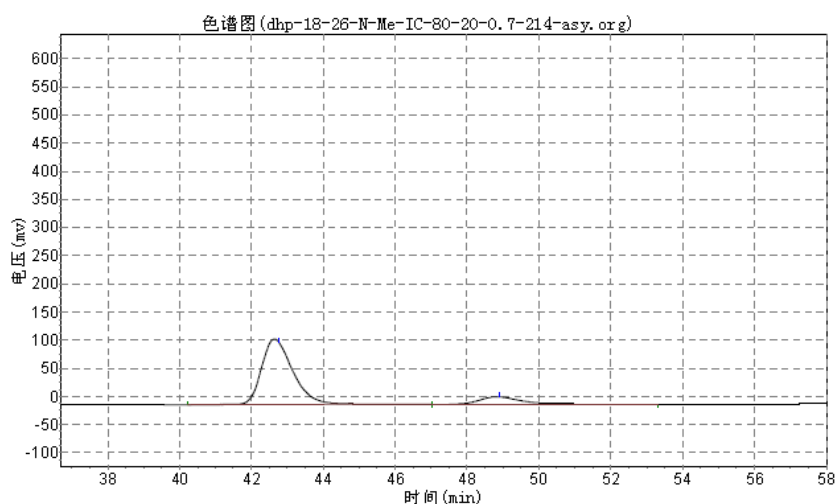
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实验者:

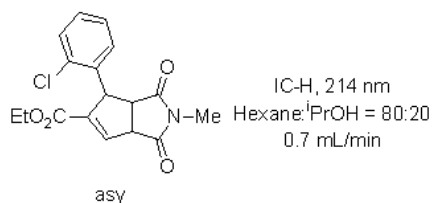
报告时间: 2011-11-18, 22:17:38

积分方法: 面积归一法

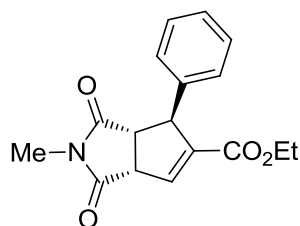


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		42.765	114180.750	6967741.500	86.6999
2		48.898	12949.637	1068876.625	13.3001
总计			127130.387	8036618.125	100.0000



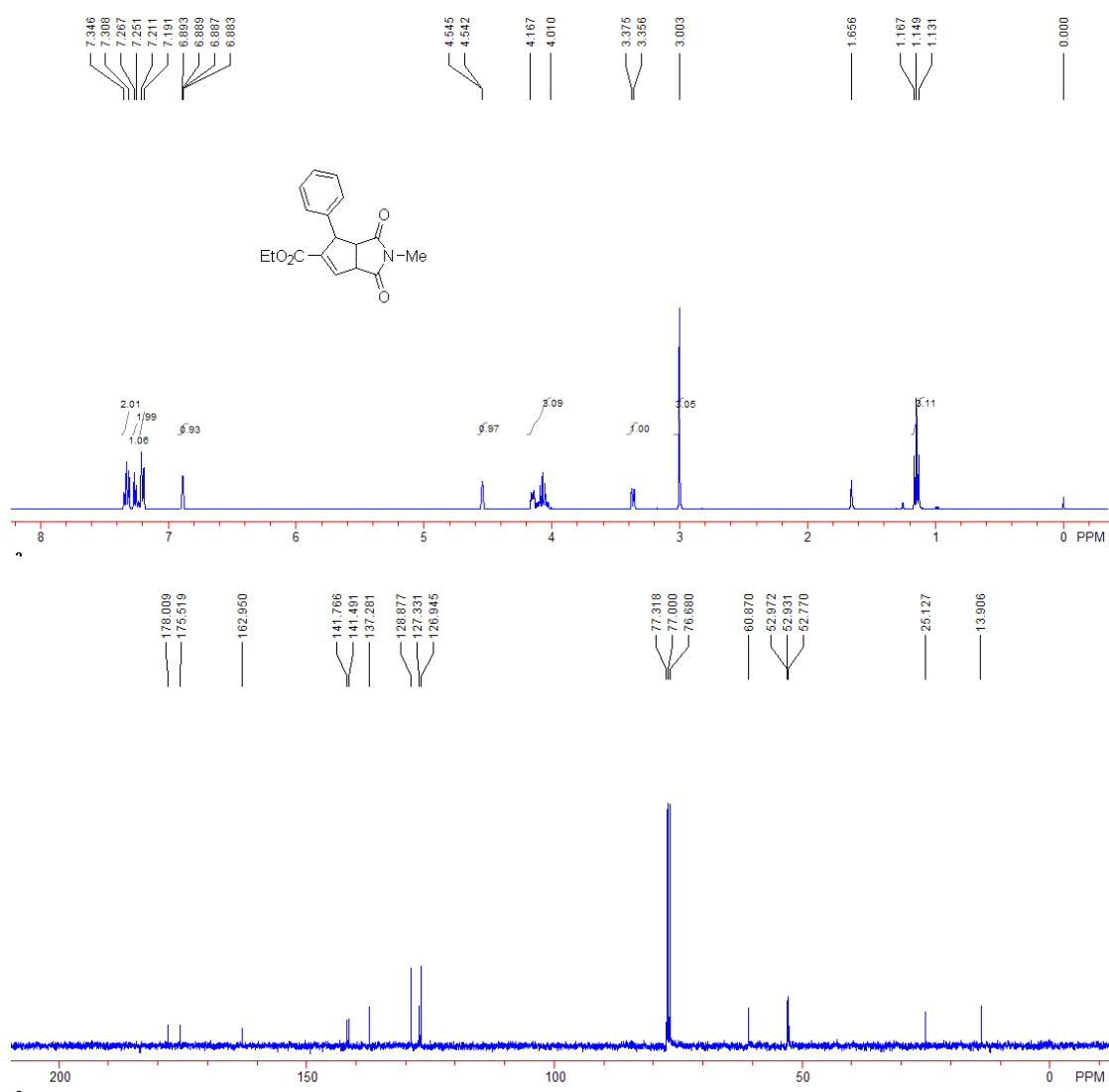
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 42.76$ min, $t_{\text{minor}} = 48.89$ min; ee = 73%; $[\alpha]_{\text{D}}^{20} = +245.6$ (c 1.0, CHCl_3)].



(3aR,4S,6aS)-ethyl

2-methyl-1,3-dioxo-4-phenyl-1,2,3,3a,4,6a-hexahydrocyclopenta[*c*]pyrrole-5-carboxylate (3m). Yield: 22 mg, 74%; colorless oil; IR (CH_2Cl_2): ν 3029, 2981,

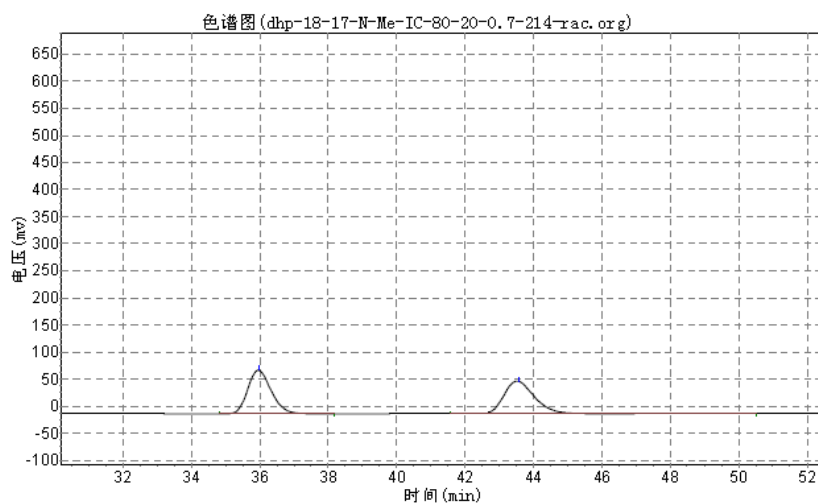
1781, 1705, 1634, 1601, 1558, 1540, 1506, 1495, 1454, 1433, 1379, 1329, 1272, 1202, 1127, 1095, 1045, 997, 959, 889, 872, 793, 761, 736, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.15 (3H, t, $J = 7.2$ Hz, CH_3), 3.00 (3H, s, CH_3), 3.37 (1H, d, $J = 7.6$ Hz, CH), 4.01–4.17 (3H, m, $\text{CH} + \text{CH}_2$), 4.54 (1H, d, $J = 1.6$ Hz, CH), 6.89 (1H, dd, $J = 1.6, 2.4$ Hz, CH), 7.20 (2H, d, $J = 8.0$ Hz, ArH), 7.25–7.27 (1H, m, ArH), 7.31–7.35 (2H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 25.1, 52.8, 52.9, 53.0, 60.9, 126.9, 127.3, 128.9, 137.3, 141.5, 141.8, 163.0, 175.5, 178.0; MS (ESI) m/z (%): 300.1 (100) $[\text{M}^+ + 1]$; HRMS (MALDI) Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_4\text{Na}$ ($\text{M}^+ + \text{Na}$) requires 322.1050, found: 322.1053; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 35.87$ min, $t_{\text{minor}} = 43.68$ min; ee = 95%; $[\alpha]_{\text{D}}^{20} = +276.5$ (c 1.0, CHCl_3)].



实验时间: 2011-09-09, 15:45:23

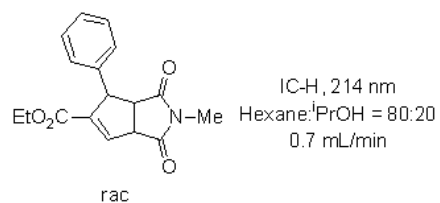
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实验者:

报告时间: 2011-11-18, 22:12:30
积分方法: 面积归一法

分析结果表

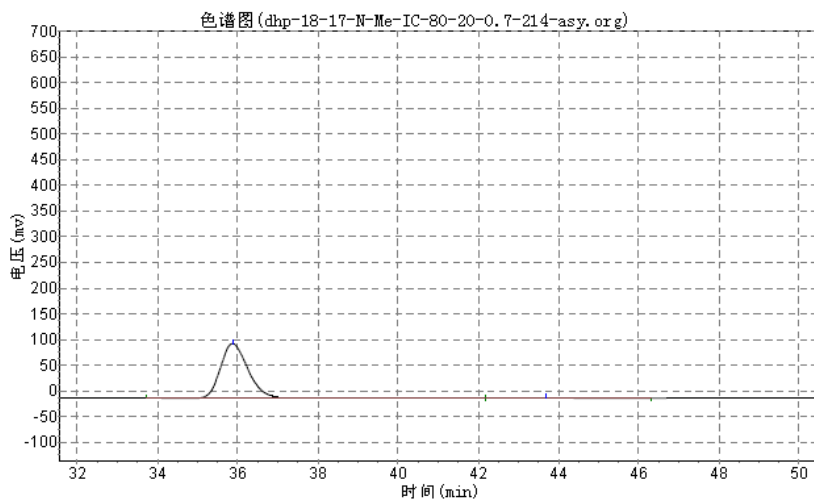
峰号	峰名	保留时间	峰高	峰面积	含量
1		35.965	80659.461	3909325.500	50.2041
2		43.565	60477.879	3877546.500	49.7959
总计			141137.340	7786872.000	100.0000



实验时间: 2011-09-09, 16:48:44

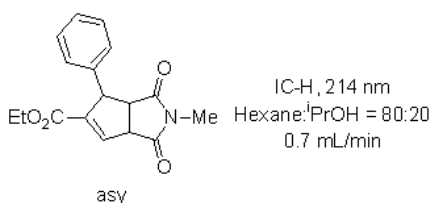
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实验者:

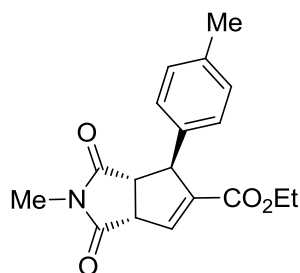
报告时间: 2011-11-18, 22:13:15
积分方法: 面积归一法

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		35.873	106873.508	5156261.500	97.2786
2		43.682	2095.773	144247.609	2.7214
总计			108969.281	5300509.109	100.0000



Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 35.87$ min, $t_{\text{minor}} = 43.68$ min; ee = 95%; $[\alpha]_{\text{D}}^{20} = +276.5$ (c 1.0, CHCl_3)].

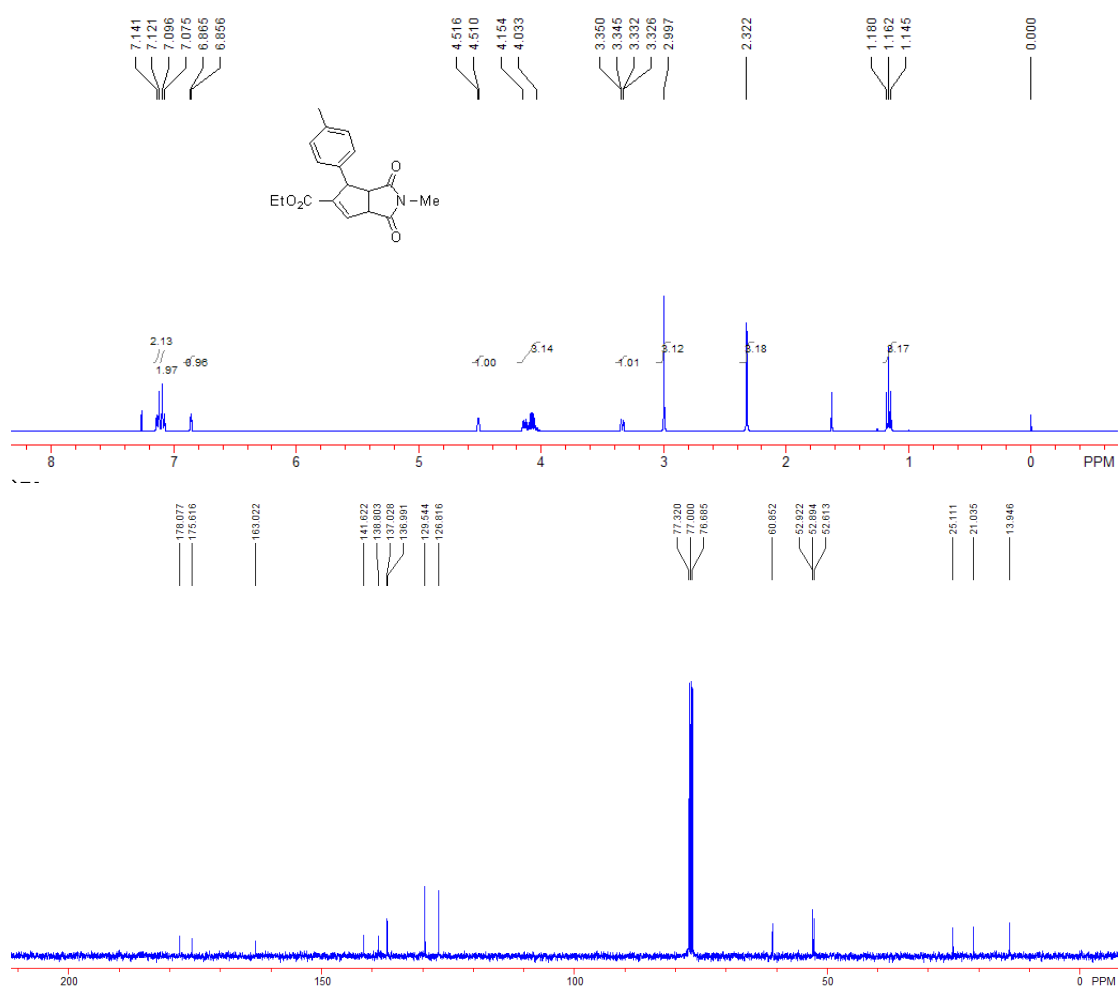


(3aR,4S,6aS)-ethyl

2-methyl-1,3-dioxo-4-(p-tolyl)-1,2,3,3a,4,6a-hexahydrocyclo-

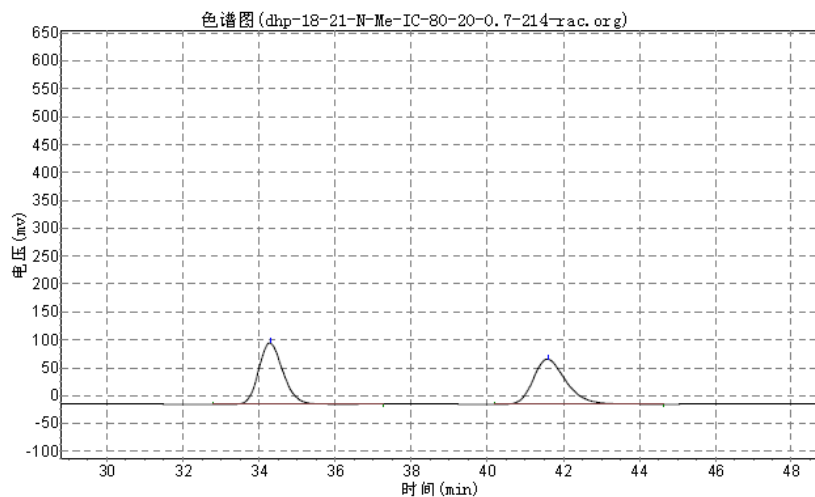
penta[c]pyrrole-5-carboxylate (3n). Yield: 20 mg, 64%; colorless oil; IR (CH_2Cl_2): ν 2981, 1780,

1705, 1653, 1634, 1558, 1540, 1513, 1433, 1379, 1327, 1271, 1201, 1126, 1094, 1045, 1000, 959, 819, 786, 739, 721 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.16 (3H, t, $J = 7.2$ Hz, CH_3), 2.32 (3H, s, CH_3), 3.00 (3H, s, CH_3), 3.34 (1H, dd, $J = 2.0, 7.2$ Hz, CH), 4.03–4.15 (3H, m, CH+ CH_2), 4.51 (1H, d, $J = 2.4$ Hz, CH), 6.86–6.87 (1H, m, CH), 7.09 (2H, d, $J = 8.0$ Hz, ArH), 7.13 (2H, d, $J = 8.0$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 13.9, 21.0, 25.1, 52.6, 52.89, 52.92, 60.8, 126.8, 129.5, 136.99, 137.03, 138.8, 141.6, 163.0, 175.6, 178.1; MS (ESI) m/z (%): 314.1 (100) [$\text{M}^+ + 1$]; HRMS (MALDI) Calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{Na}$ ($\text{M}^+ + \text{Na}$) requires 336.1206, found: 336.1207; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 33.94$ min, $t_{\text{minor}} = 41.40$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +258.2$ (c 1.0, CHCl_3)].



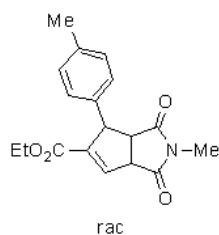
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实验者:
报告时间: 2011-11-18, 22:10:12
积分方法: 面积归一法



分析结果表

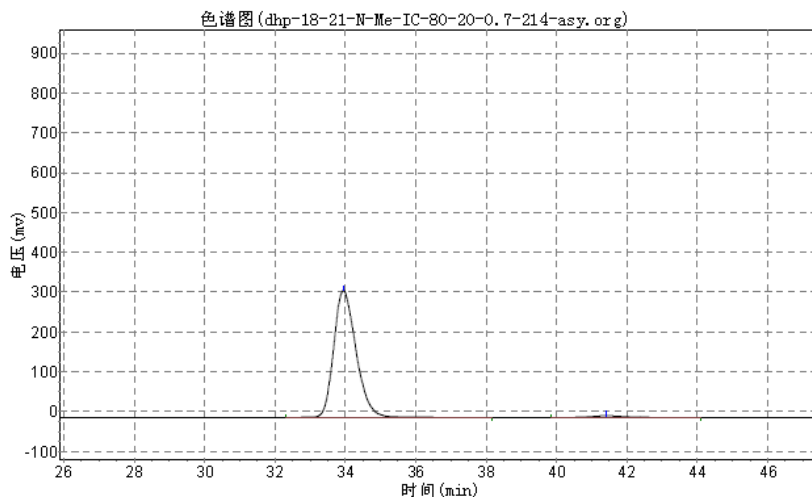
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1		34.290	110073.250	4924989.000	50.3600
2		41.590	80951.609	4854581.000	49.6400
总计			191024.859	9779570.000	100.0000



IC-H, 214 nm
Hexane: iPrOH = 80:20
0.7 mL/min

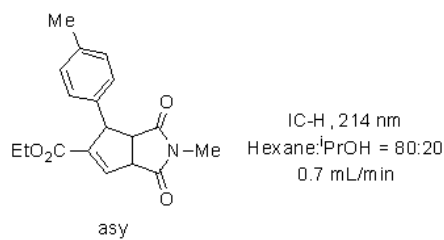
实验时间: 2011-09-14, 19:43:27
谱图文件: E:\实验数据\HPLC\dhp\dhp-18-21-N-Me-IC-80-20-0.7-214-asy.org

实验者:
报告时间: 2011-11-18, 22:10:58
积分方法: 面积归一法

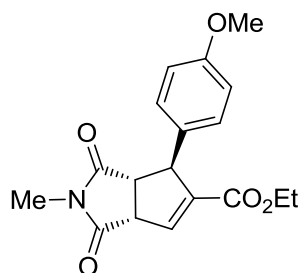


分析结果表

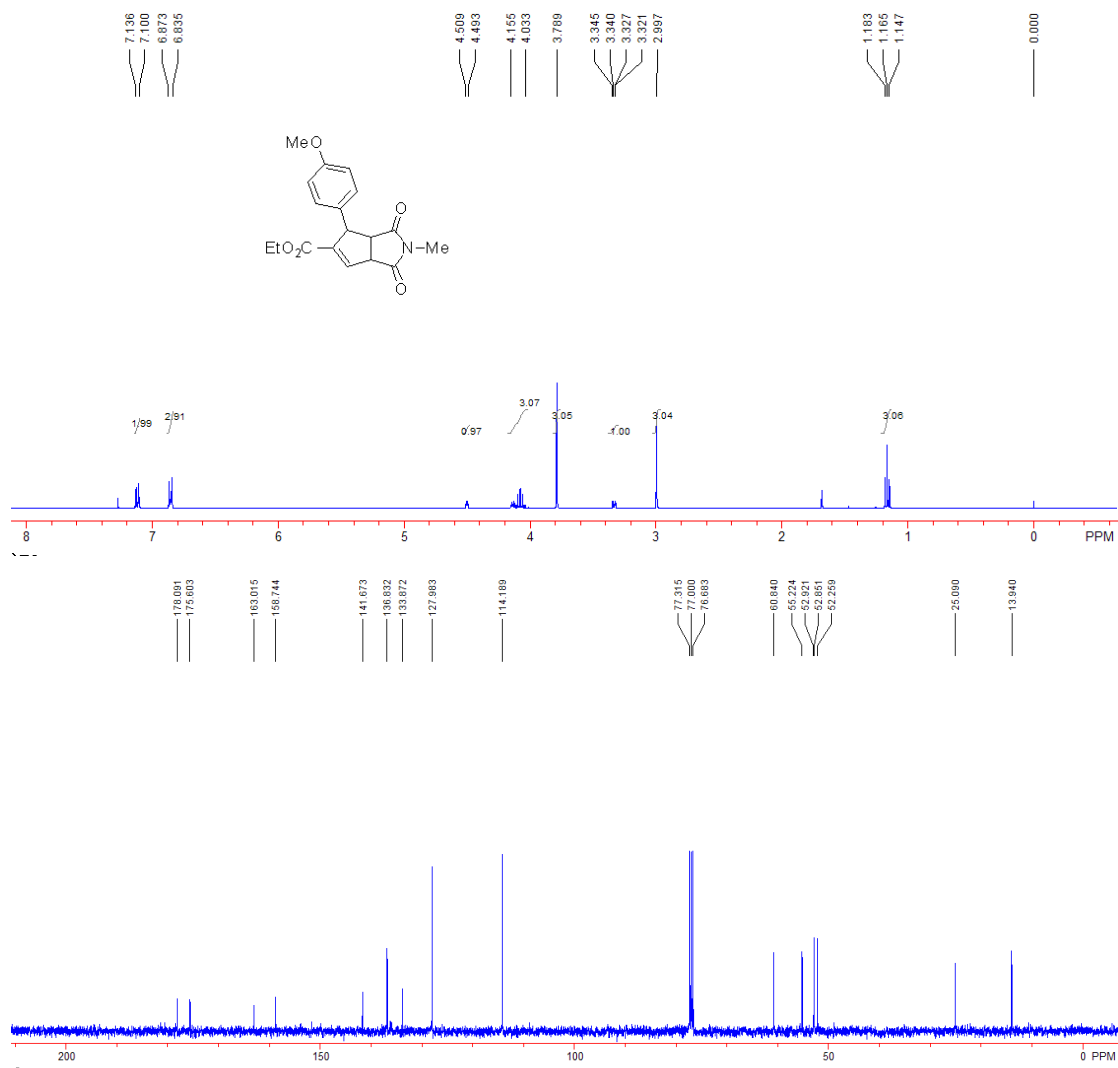
峰号	峰名	保留时间	峰高	峰面积	含量
1		33.947	318548.594	14097616.000	97.9174
2		41.407	4603.955	299846.406	2.0826
总计			323152.549	14397462.406	100.0000



Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 80/20; flow rate: 0.7 mL/min; $t_{\text{major}} = 33.94$ min, $t_{\text{minor}} = 41.40$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +258.2$ (c 1.0, CHCl_3)].



(3a*R*,4*S*,6a*S*)-ethyl 4-(4-methoxyphenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6ahexahydrocyclopenta[*c*]pyrrole-5-carboxylate (3o). Yield: 18 mg, 55%; colorless oil; IR (CH₂Cl₂): ν 2937, 1780, 1704, 1632, 1610, 1512, 1433, 1379, 1274, 1203, 1178, 1126, 1094, 1033, 1000, 959, 833, 794, 727 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.16 (3H, t, *J* = 7.2 Hz, CH₃), 3.00 (3H, s, CH₃), 3.33 (1H, dd, *J* = 2.0, 7.2 Hz, CH), 3.79 (3H, s, CH₃), 4.03–4.16 (3H, m, CH+CH₂), 4.49–4.51 (1H, m, CH), 6.84–6.87 (3H, m, CH+ArH), 7.10–7.14 (2H, m, ArH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.9, 25.1, 52.2, 52.8, 52.9, 55.2, 60.8, 114.2, 128.0, 133.9, 136.8, 141.7, 158.7, 163.0, 175.6, 178.1; MS (ESI) *m/z* (%): 330.1 (100) [M⁺ + 1]; HRMS (MALDI) Calcd. for C₁₈H₁₉NO₅Na (M⁺ + Na) requires 352.1156, found: 352.1145; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [λ = 214 nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; *t*_{major} = 23.56 min, *t*_{minor} = 34.64 min; ee = 96%; [α]_D²⁰ = +273.1 (*c* 1.0, CHCl₃)].



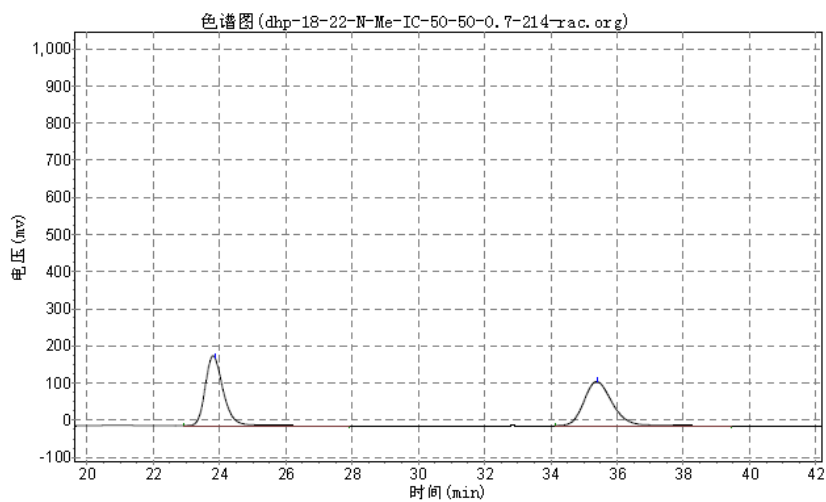
实验时间: 2011-09-14, 22:47:06

谱图文件:E:\实验数据\HPLC\dhp\dhp-18-22-N-Me-IC-50-50-0.7-214-rac.org

实验者:

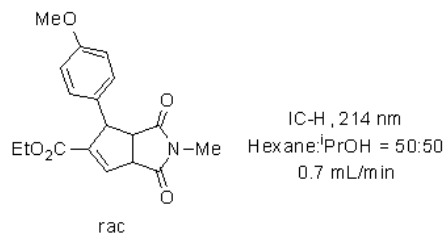
报告时间: 2011-11-18, 22:13:58

积分方法: 面积归一法



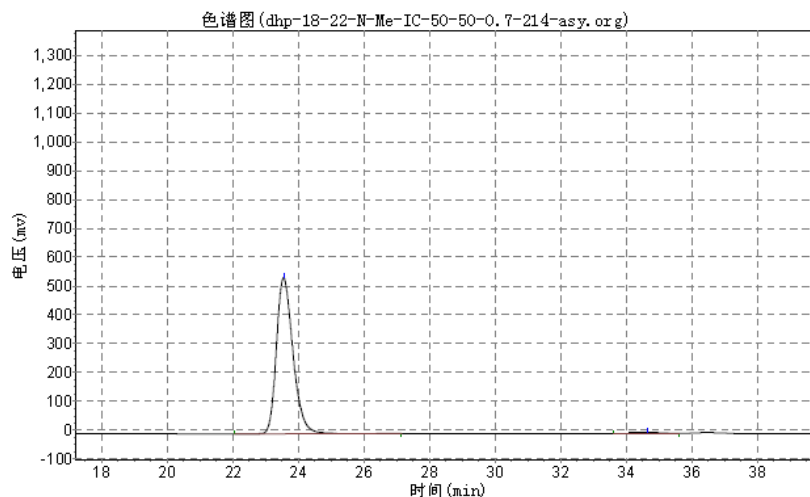
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		23.857	186342.219	7031739.500	50.0084
2		35.390	118534.805	7029379.500	49.9916
总计			304877.023	14061119.000	100.0000



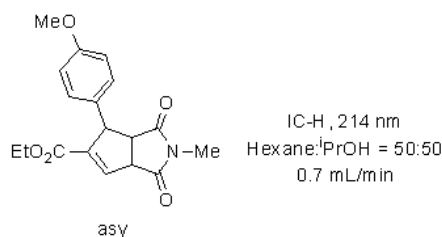
实验时间: 2011-09-14, 23:40:34
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实验者:
 报告时间: 2011-11-18, 22:14:52
 积分方法: 面积归一法

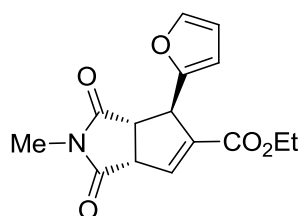


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		23.555	541739.313	19044796.000	98.7160
2		34.640	4509.533	247716.656	1.2840
总计			546248.845	19292512.656	100.0000

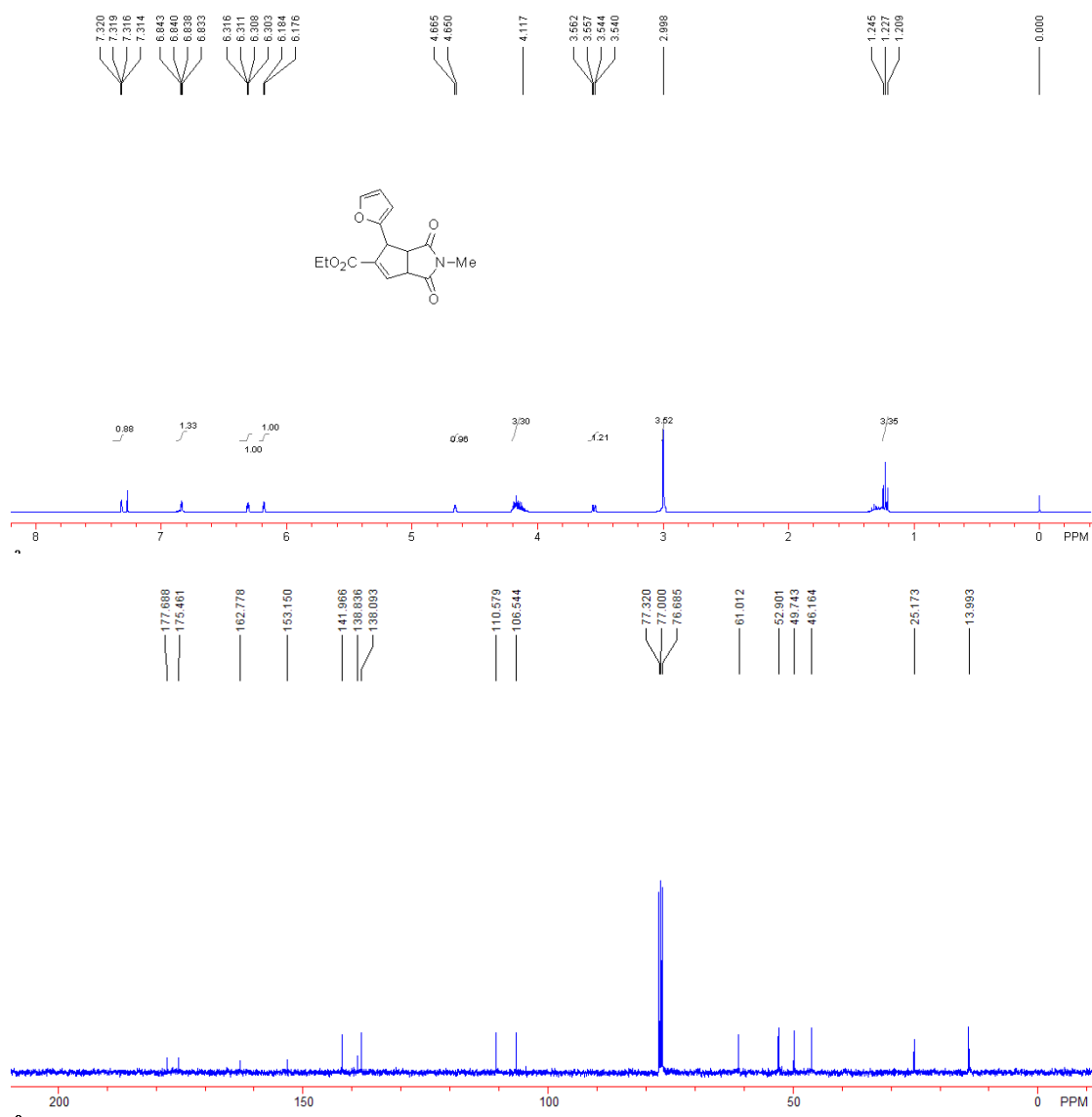


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 23.56$ min, $t_{\text{minor}} = 34.64$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +273.1$ (c 1.0, CHCl_3)].



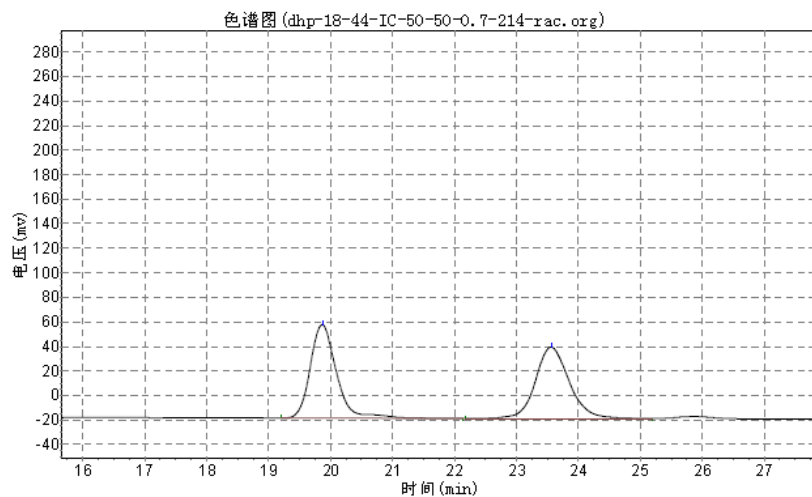
(3a*R*,4*R*,6a*S*)-ethyl 4-(furan-2-yl)-2-methyl-1,3-dioxo-1,2,3,3a,4,6a-hexahydrocyclopenta[c]pyrrole-5-carboxylate (3p). Yield: 26 mg, 69%; yellow oil; IR (CH_2Cl_2): ν 2982, 1780,

1704, 1635, 1505, 1434, 1380, 1282, 1195, 1127, 1096, 1013, 959, 893, 856, 791, 738 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.23 (3H, t, $J = 7.2$ Hz, CH_3), 3.00 (3H, s, CH_3), 3.55 (1H, dd, $J = 2.0, 7.2$ Hz, CH), 4.04–4.15 (3H, m, CH+ CH_2), 4.60 (1H, d, $J = 2.0$ Hz, CH), 6.18 (1H, d, $J = 3.2$ Hz, ArH), 6.32 (1H, dd, $J = 2.0, 3.2$ Hz, CH), 6.83–6.84 (1H, m, ArH), 7.31–7.32 (1H, m, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 14.0, 25.2, 46.2, 49.7, 52.9, 61.0, 106.5, 110.6, 138.1, 138.8, 142.0, 153.2, 162.8, 175.5, 177.7; MS (ESI) m/z (%): 290.0 (100) [$\text{M}^+ + 1$]; HRMS (ESI) Calcd. for $\text{C}_{15}\text{H}_{15}\text{NNaO}_5$ ($\text{M}^+ + \text{Na}$) requires 312.0842, found: 312.0836; Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 19.80$ min, $t_{\text{minor}} = 23.53$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +240.8$ (c 1.0, CHCl_3)].



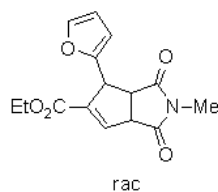
实验时间: 2011-10-21, 10:43:14
谱图文件: E:\实验数据\HPLC\dhp\dhp-18-44-IC-50-50-0.7-214-
rac.org

实验者:
报告时间: 2011-11-26, 10:54:42
积分方法: 面积归一法



分析结果表

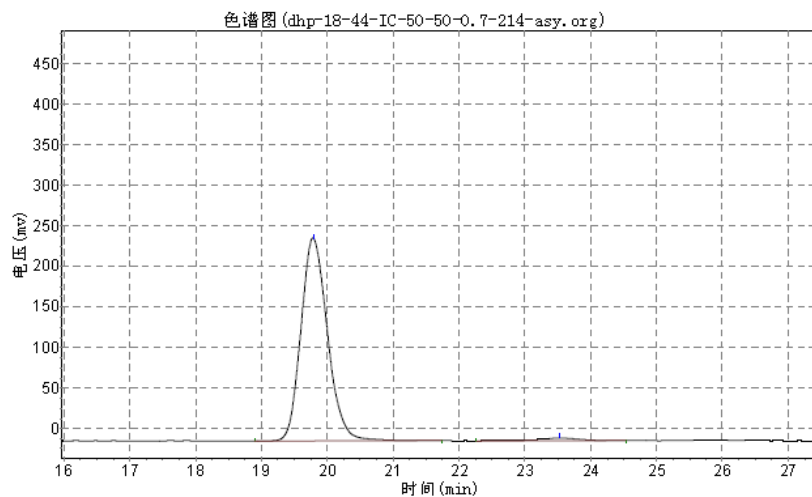
峰号	峰名	保留时间	峰高	峰面积	含量
1		19.865	75889.680	2232837.000	50.1217
2		23.565	58237.262	2221996.250	49.8783
总计			134126.941	4454833.250	100.0000



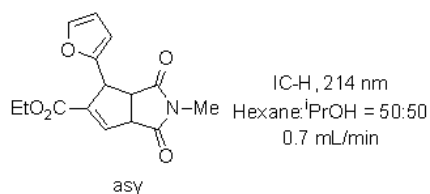
IC-H, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

实验时间: 2011-10-21, 11:24:11
谱图文件: E:\实验数据\HPLC\dhp\18-44-IC-50-50-0.7-214-asy.org

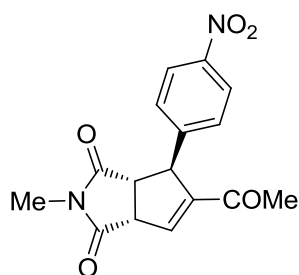
实验者:
报告时间: 2011-11-26, 10:56:55
积分方法: 面积归一法



分析结果表					
峰号	峰名	保留时间	峰高	峰面积	含量
1		19.798	250046.594	7008134.500	97.8119
2		23.532	3327.882	156772.406	2.1881
总计			253374.476	7164906.906	100.0000

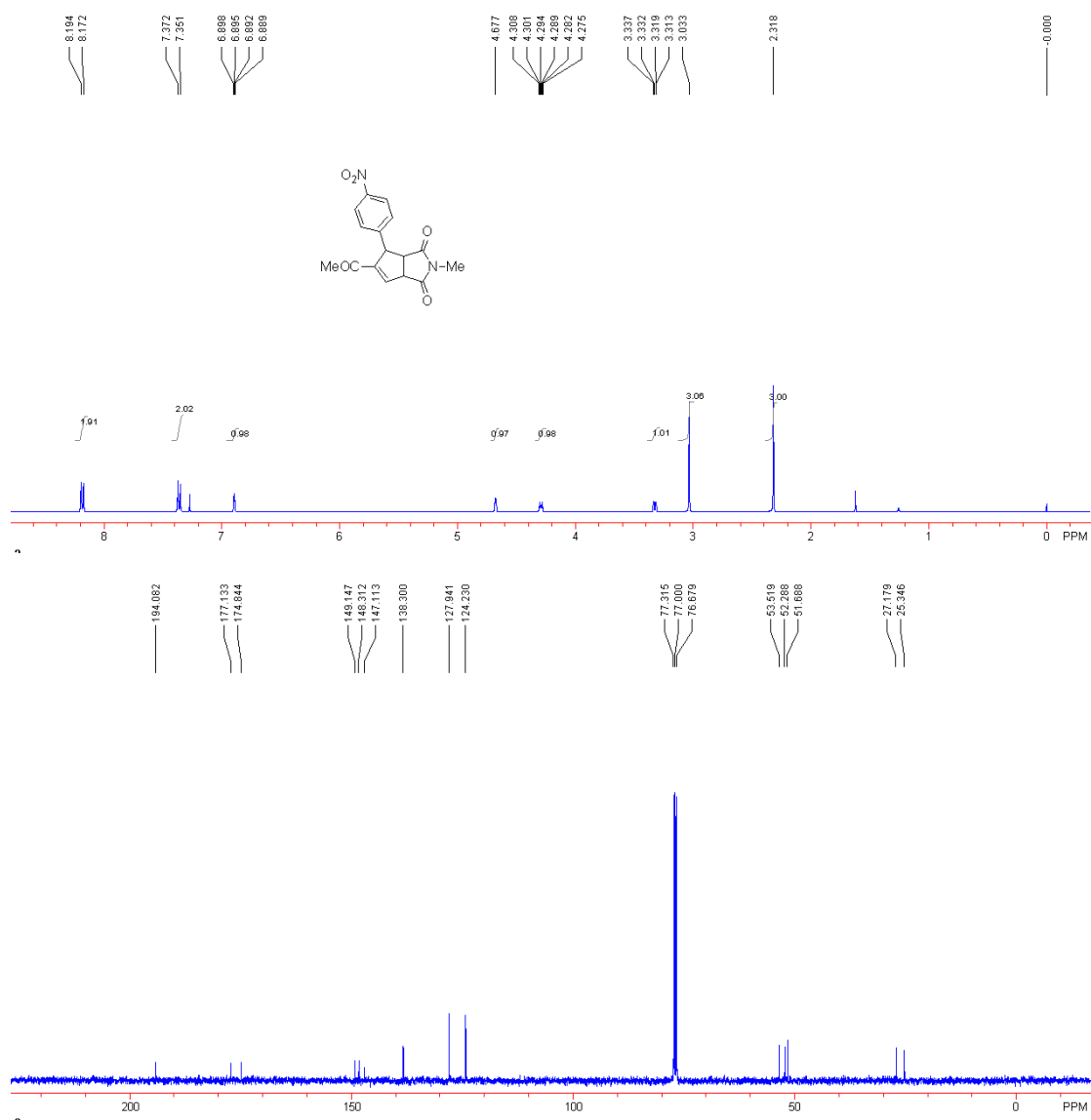


Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel IC-H column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 19.80$ min, $t_{\text{minor}} = 23.53$ min; ee = 96%; $[\alpha]_{\text{D}}^{20} = +240.8$ (c 1.0, CHCl_3)].



(3aS,6S,6aR)-5-acetyl-2-methyl-6-(4-nitrophenyl)-6,6a-dihydrocyclopenta[c]pyrrole-1,3(2H,3H)-dione (**3q**). Yield: 32 mg, >99%; colorless solid, mp 268–272 °C; IR (CH_2Cl_2): ν 2957,

2927, 2858, 1780, 1701, 1668, 1596, 1514, 1433, 1347, 1280, 1124, 1058, 1011, 963, 851, 809, 756, 740, 705, 640 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , TMS): δ 2.32 (3H, s, CH_3), 3.03 (3H, s, CH_3) 3.33 (1H, dd, $J = 2.0, 7.2$ Hz, CH), 4.28–4.31 (1H, m, CH), 4.65–4.68 (1H, m, CH), 6.89 (1H, dd, $J = 1.2, 2.0$ Hz, CH), 7.36 (2H, d, $J = 8.4$ Hz, ArH), 8.18 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ 25.3, 27.2, 51.7, 52.3, 53.5, 124.2, 127.9, 138.3, 147.1, 148.3, 149.1, 174.8, 177.1, 194.1; MS (ESI) m/z (%): 315.0 (100) [$\text{M}^+ + 1$]; HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{NaO}_5$ ($\text{M}^+ + \text{Na}$) requires 337.0795, found: 337.0793; Enantiomeric excess was determined by HPLC with a Chiralcel PA-2 column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 47.66$ min, $t_{\text{minor}} = 70.64$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +389.8$ (c 1.0, CHCl_3)].



实验时间: 2012-01-14, 12:07:09

谱图文件: E:\实验数据\HPLC\dhp\19-70-sub1-PA-2-50-50-0.7-214-rac-re.org

实验者:

报告时间: 2012-01-16, 15:44:44

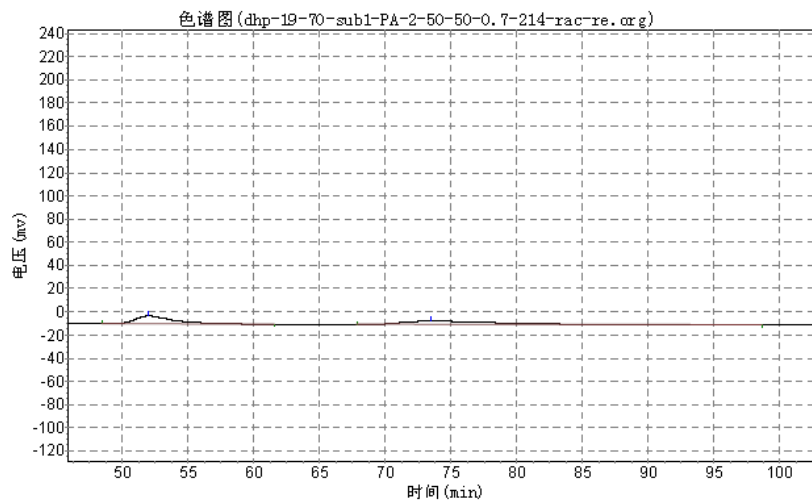
积分方法: 面积归一法

使用仪器类型: 气相色谱

检测器: FID

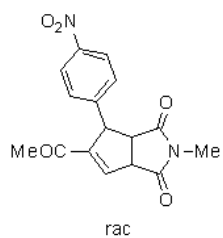
进样器: 分流

柱温: 程序升温



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		51.985	6634.631	1377864.750	49.0344
2		73.472	2890.285	1432131.500	50.9656
总计			9524.916	2809996.250	100.0000



PA-2, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

实验时间: 2012-01-14, 14:28:13

谱图文件: E:\实验数据\HPLC\dhp\19-70-sub1-PA-2-50-50-0.7-214-asy.org

实验者:

报告时间: 2012-01-16, 15:40:53

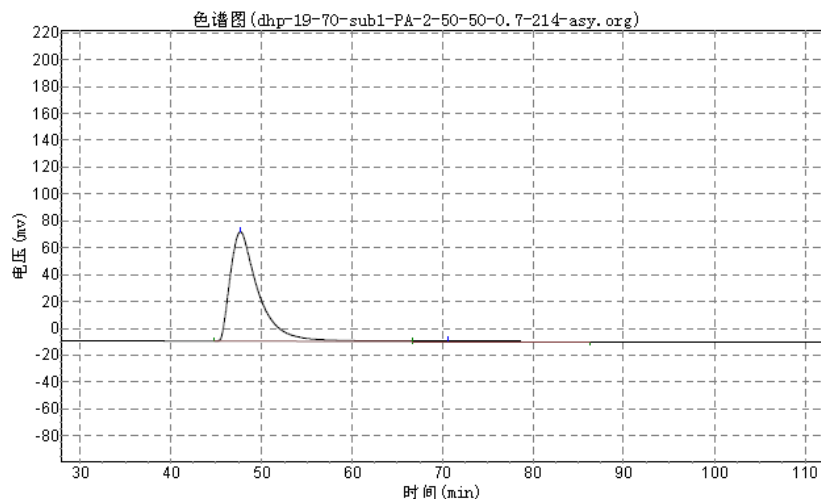
积分方法: 面积归一法

使用仪器类型: 气相色谱

检测器: FID

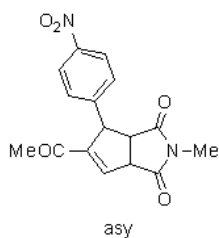
进样器: 分流

柱温: 程序升温



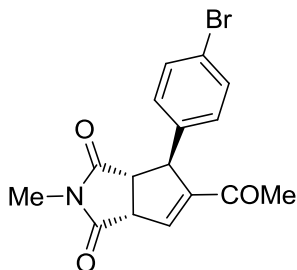
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		47.662	81543.414	17458990.000	98.3125
2		70.643	676.247	299673.844	1.6875
总计			82219.661	17758663.844	100.0000

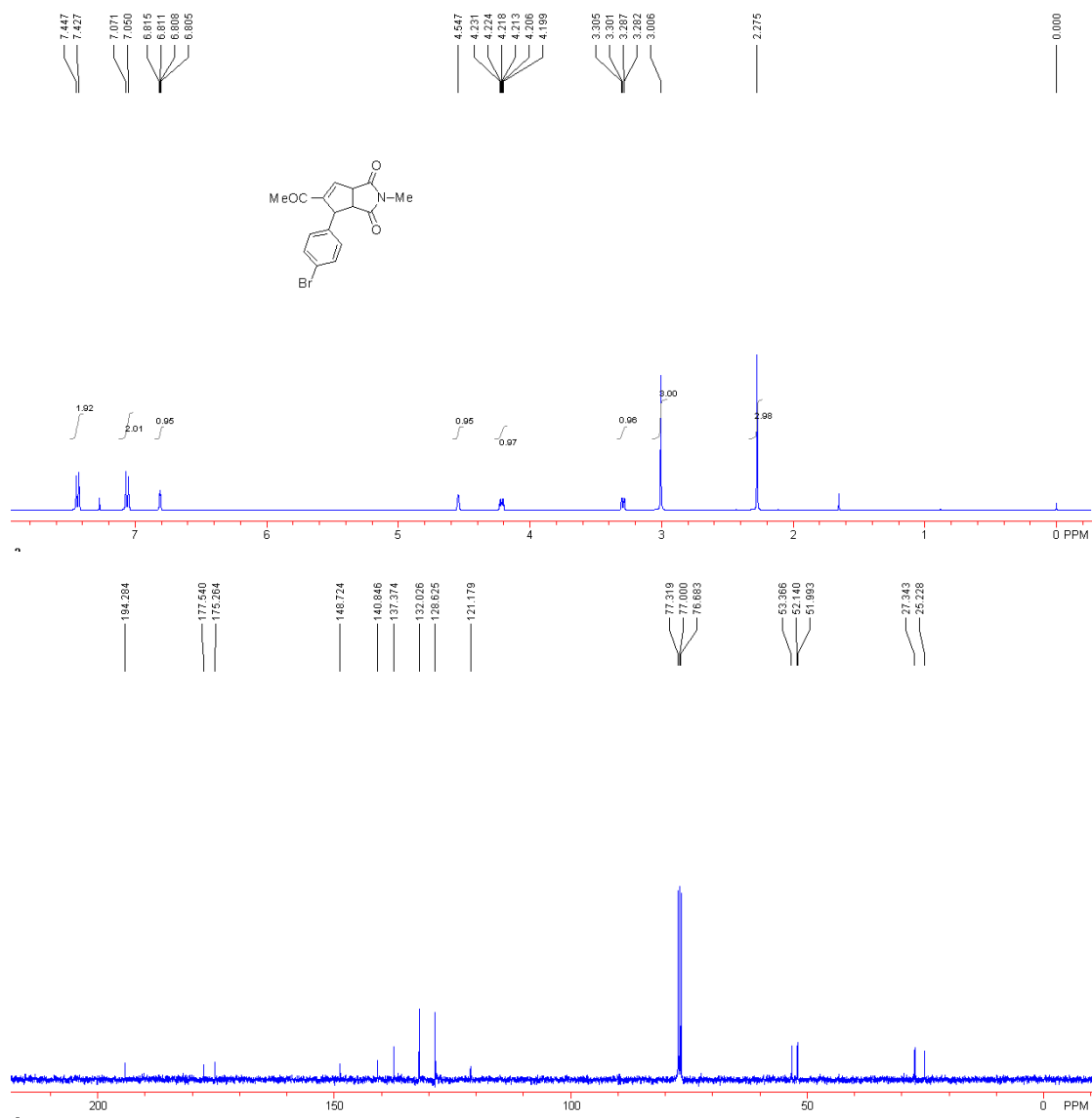


PA-2, 214 nm
Hexane: iPrOH = 50:50
0.7 mL/min

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel PA-2 column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 47.66$ min, $t_{\text{minor}} = 70.64$ min; ee = 97%; $[\alpha]_{\text{D}}^{20} = +389.8$ (c 1.0, CHCl_3)].



(3a*S*,6*S*,6a*R*)-5-acetyl-6-(4-bromophenyl)-2-methyl-6,6a-dihydrocyclopenta[*c*]pyrrole-1,3(2*H*,3a*H*)-dione (3o). Yield: 32 mg, 92%; colorless solid, mp 185–189 °C; IR (CH₂Cl₂): ν 3072, 2950, 2926, 1780, 1701, 1677, 1616, 1487, 1432, 1380, 1282, 1127, 1072, 1010, 962, 893, 825, 744 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.28 (3H, s, CH₃), 3.01 (3H, s, CH₃) 3.29 (1H, dd, *J* = 1.6, 7.2 Hz, CH), 4.20–4.23 (1H, m, CH), 4.53–4.56 (1H, m, CH), 6.89 (1H, dd, *J* = 1.6, 2.8 Hz, CH), 7.06 (2H, d, *J* = 8.4 Hz, ArH), 7.44 (2H, d, *J* = 8.4 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 25.2, 27.3, 52.0, 52.1, 53.4, 121.2, 128.6, 132.0, 137.4, 140.8, 148.7, 175.3, 177.5, 194.3; MS (ESI) *m/z* (%): 348.0 (100) [*M*⁺ + 1]; HRMS (ESI) Calcd. for C₁₆H₁₄BrNNaO₃ (*M*⁺ + Na) requires 370.0049, found: 370.0037; Enantiomeric excess was determined by HPLC with a Chiralcel PA-2 column [λ = 214 nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; *t*_{major} = 17.12 min, *t*_{minor} = 24.92 min; ee = 98%; [α]_D²⁰ = +360.6 (*c* 1.0, CHCl₃)].



HPLC Report

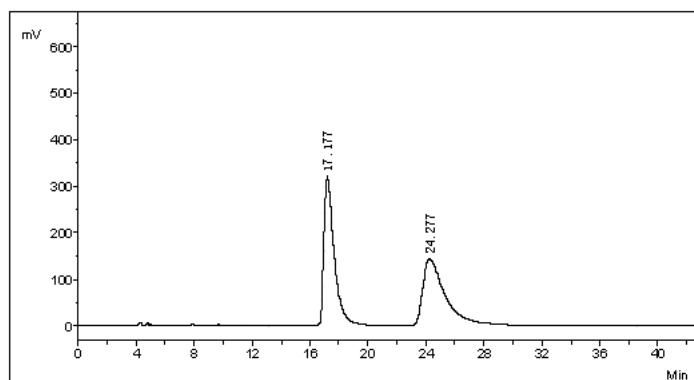
Sample Name:

Data File:Dhp-19-70-sub2-rac PA-2 55 214 0.7. che

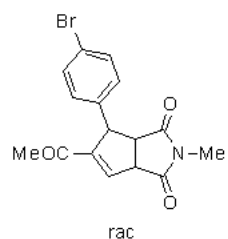
Operator:

Date:2012-01-13

Time:15:35



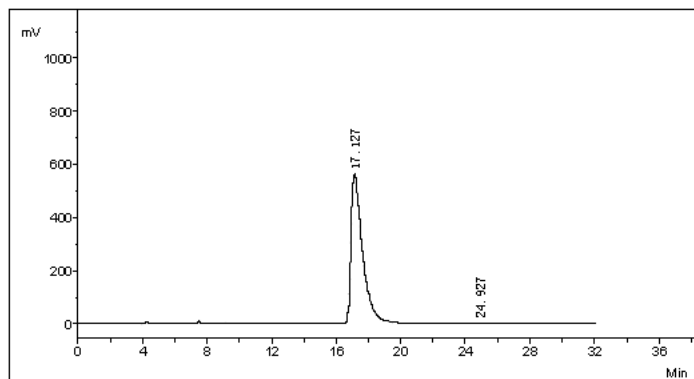
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		17.177	320400.0	16081475.9	50.8485
2	2		24.277	143764.6	15544750.1	49.1515
Total				464164.6	31626226.0	100.0000



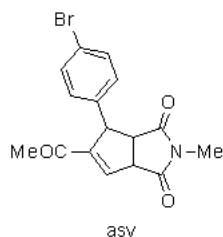
PA-2, 214 nm
Hexane:PrOH = 50:50
0.7 mL/min

HPLC Report

Sample Name: Data File:Dhp-19-70-sub2-asy PA-2 55 214 0.7.che
 Operator: Date:2012-01-13
 Time:16:20



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		17.127	562022.2	28294438.9	99.1938
2	2		24.927	2200.4	229976.4	0.8062
Total				564222.6	28524415.3	100.0000



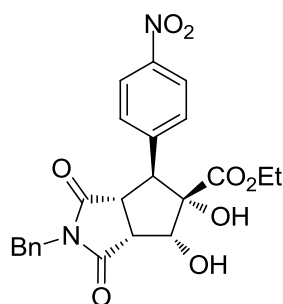
PA-2, 214 nm
 Hexane:PrOH = 50:50
 0.7 mL/min

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralcel PA-2 column [$\lambda = 214$ nm; eluent: hexane/isopropanol 50/50; flow rate: 0.7 mL/min; $t_{\text{major}} = 17.12$ min, $t_{\text{minor}} = 24.92$ min; ee = 98%; $[\alpha]_{\text{D}}^{20} = +360.6$ (c 1.0, CHCl_3)].

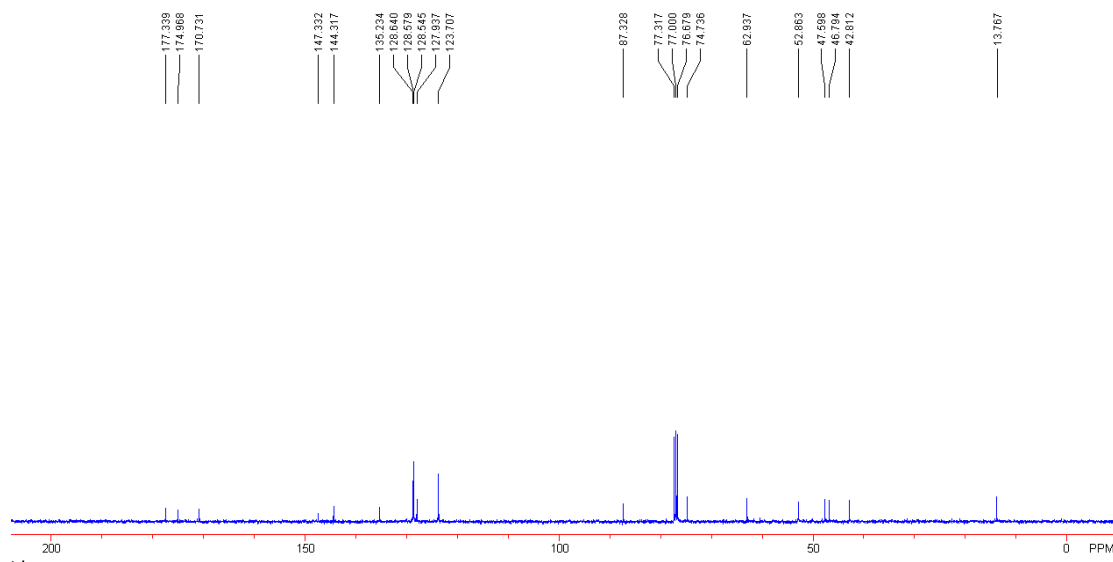
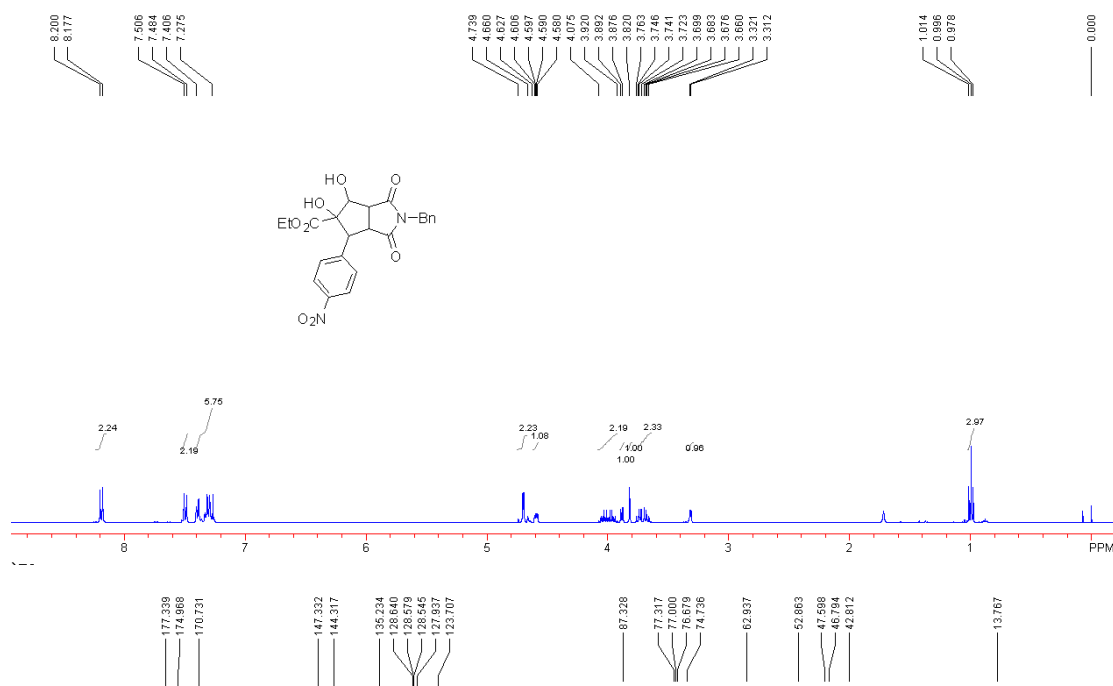
2. General procedure for the dihydroxylation of **4c** [2,3].

General Procedure: NaIO_4 (0.16 mmol, 34 mg, 2 equiv) and distilled water (0.1 mL) were added to a flask. After the NaIO_4 had been dissolved, the solution was cooled to 0 °C, and two drops of H_2SO_4 aqueous (2 M) was added and stirred for 5 min. Then $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.008 mmol, 3.0 mg, 0.1 equiv) was added, followed by two drops of H_2SO_4 aqueous (2 M). The resulting solution was stirred for 5 min, and then EtOAc (0.2 mL) was added. After the solution had been stirred for 5 min, CH_3CN (0.3 mL) was added. The solution was stirred for 5 min, and then a solution of substrate **3c** (0.08 mmol,

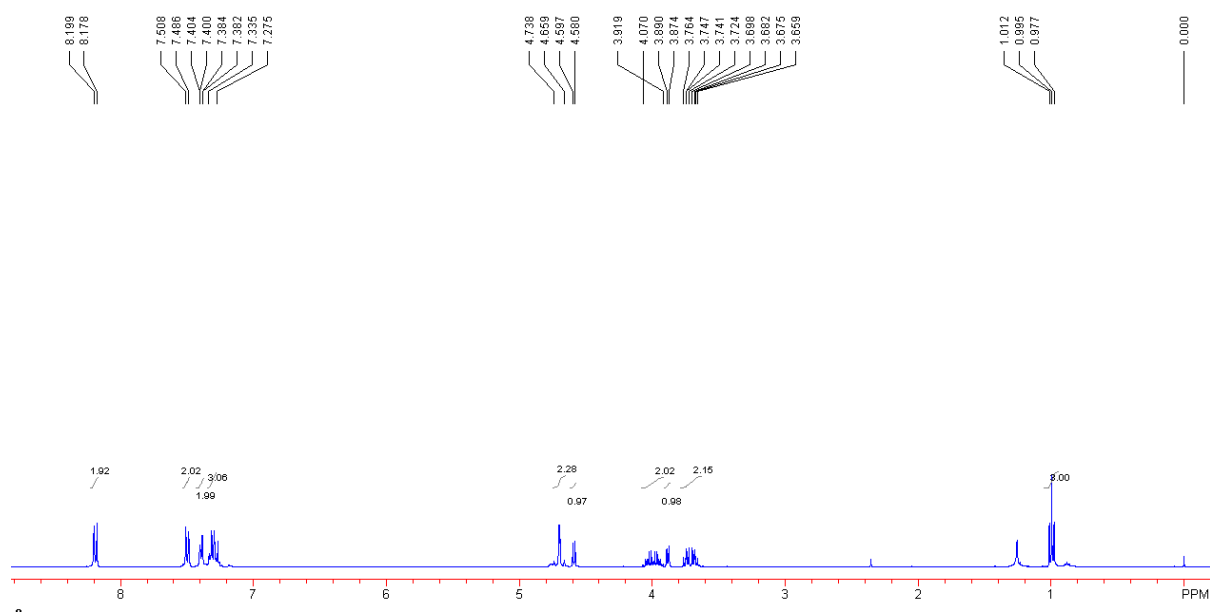
34 mg) in EtOAc (0.3 mL) was added. The solution was further stirred for 10 min, and then 10% NaHCO₃ (0.7 mL) and saturated Na₂SO₃ solution (2.5 mL) were added. After the solution had been stirred for 30 min at room temperature, it was extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and the solvent was removed under reduced pressure and residue was chromatographed on silica gel (elution with petroleum ether/EtOAc 2:1) to provide compound **4c**.



(3aR,4R,5S,6S,6aR)-ethyl 2-benzyl-4,5-dihydroxy-6-(4-nitrophenyl)-1,3-dioxooctahydrocyclopenta[c]pyrrole-5-carboxylate (4c). Yield: 25 mg, 69%; yellow oil; IR (CH₂Cl₂): ν 2961, 2925, 2854, 1699, 1519, 1399, 1347, 1259, 1089, 1017, 796, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.00 (3H, t, J = 7.2 Hz, CH₃), 3.32 (1H, d, J = 3.6 Hz, OH), 3.66–3.76 (2H, m, CH+CH), 3.82 (1H, s, OH), 3.88 (1H, d, J = 5.6 Hz, CH), 3.92–4.08 (2H, m, CH₂), 4.59 (1H, dd, J = 3.6, 5.6 Hz, CH), 4.63–4.74 (2H, m, CH₂), 7.28–7.41 (5H, m, ArH), 7.48–7.51 (2H, m, ArH), 8.18–8.20 (2H, m, ArH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 13.8, 42.8, 46.8, 47.6, 52.9, 62.9, 74.7, 87.3, 123.7, 127.9, 128.5, 128.58, 128.64, 135.2, 144.3, 147.3, 170.7, 175.0, 177.3; MS (MADLI) m/z (%): 477.4 (38.0) [M⁺ + Na]; HRMS (MADLI) Calcd. for C₂₃H₂₃N₂O₈ (M⁺ + 1) requires 455.1449, found: 455.1457; $[\alpha]_D^{20}$ = +73.3 (c 1.0, CHCl₃).



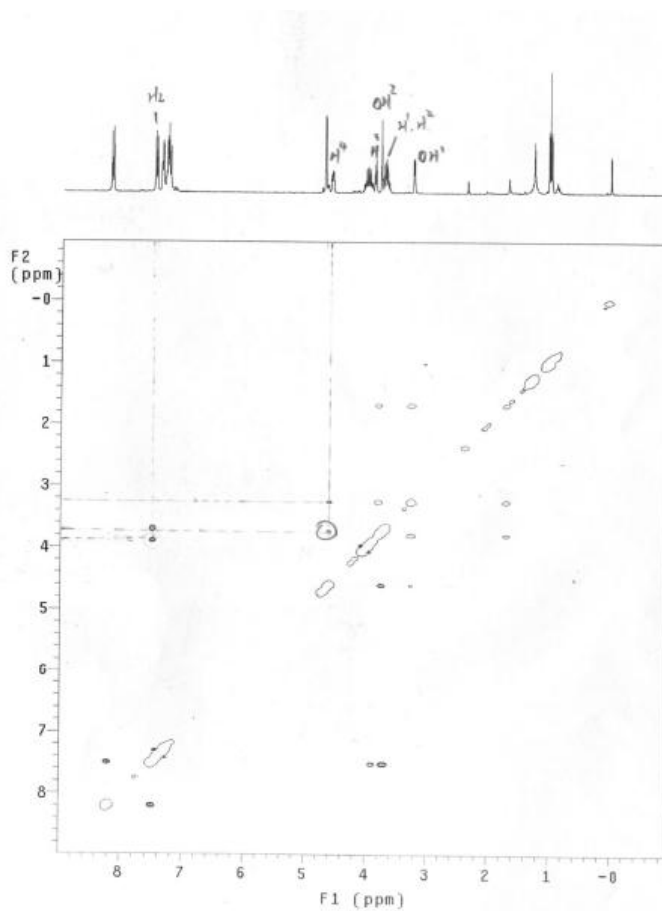
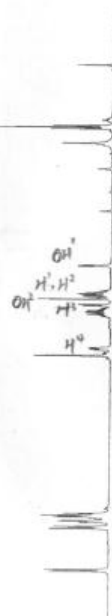
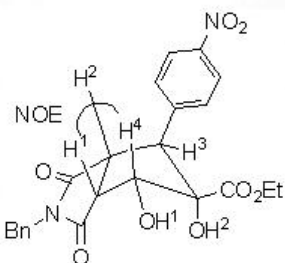
¹H NMR (400 MHz) spectroscopy of **4c** after adding D₂O into the NMR tube.



NOESY (Varian Mercury-300 MHz)

exp8 NOESY

SAMPLE		FLAGS		
date	Feb 7 2012	hs		n
solvent	CDCl3	sspu1		y
sample	dhp-19-76-r~	PFGflg		y
	8 07Feb2012	hsglvt		1043
ACQUISITION		SPECIAL		
sw	4807.7	temp	not used	
at	0.213	gain	26	
np	2048	spin	0	
fb	not used	f2	PROCESSING	
ss	32	lb	3.00	
dl	2.000	gf	0.080	
nt	32	gfs	not used	
		fn	2048	
2D ACQUISITION		F1 PROCESSING		
sw1	4807.7	gf1	0.025	
nl	128	gf51	not used	
tn	H1	proc1	1p	
sfrq	300.029	fn1	2048	
tof	264.0			
tpwr	60	sp	-282.3	
pw	8.400	wp	2976.6	
	NOESY	sp1	-294.0	
mix	0.800	wp1	2990.7	
PRESATURATION	nnnn	rf1	691.5	
satpwr	0	rf11	599.2	
satdly	0	rfp1	0	
satfrq	0			
DECOUPLER		PLOT		
dn	C13	wc	155.0	
dm	nnn	sc	10.0	
		wc2	155.0	
		sc2	0	
		vs	379	
		th	2	
		al	ph	



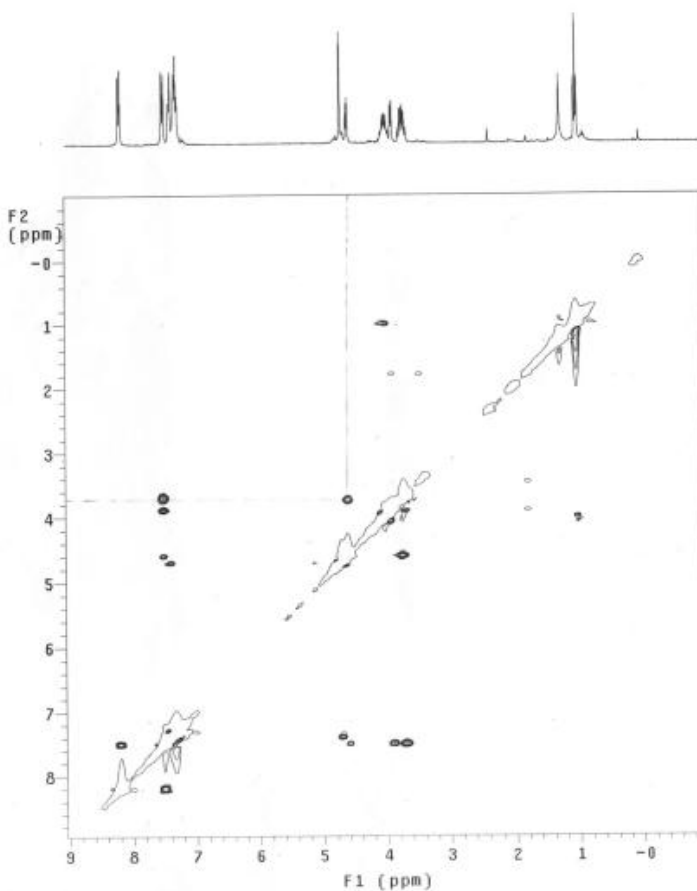
NOESY spectra of **4c** after adding D₂O into the NMR tube

exp8 NOESY

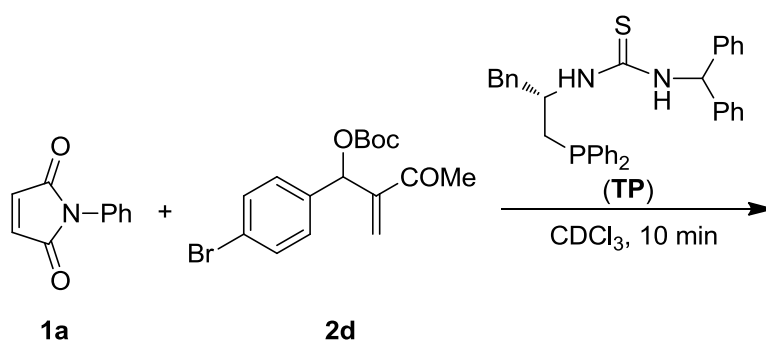
```

SAMPLE          FLAGS
date    Feb 13 2012    h8      n
solvent  CDC13         sspul    y
sample   denghp-19-7~  PFGflg   y
6-D2O    13Feb2012    hsglv1  1043
ACQUISITION          SPECIAL 1043
sw  4807.7    temp    not used
at  0.213    gain     22
np  2048     spin     0
fb  not used  F2 PROCESSING
ss  32       lb       3.00
d1  2.000    gf       0.071
nt  32       gfs     not used
2D ACQUISITION      fn  2048
sw1 4807.7    F1 PROCESSING
nl  128       gf1     0.025
TRANSMITTER          gfs1    not used
tn  H1        procl    lp
sfrq 300.025  fn1     2048
tof  264.0
tpwr 60       sp       -299.9
pw  8.400     wp       2986.0
mix  NOESY    sp1      -292.9
PRESATURATION        wp1     3004.5
satpwr 0       rfp      598.0
satdy  0       rf1      0
satfrq 0       rfp1     0
DECOUPLER            wc      155.0
dn  C13        sc       10.0
dn  nm         sc2      155.0
vs  680
th  0
al  ph
PLOT

```



3. ^{31}P NMR Spectroscopy of the control experiments



- TP (0.05 mmol)
- 1a** (0.05 mmol) and TP (0.05 mmol)
- 2d** (0.05 mmol) and TP (0.05 mmol)
- 1a** (0.05 mmol), **2d** (0.05 mmol) and TP (0.05 mmol)

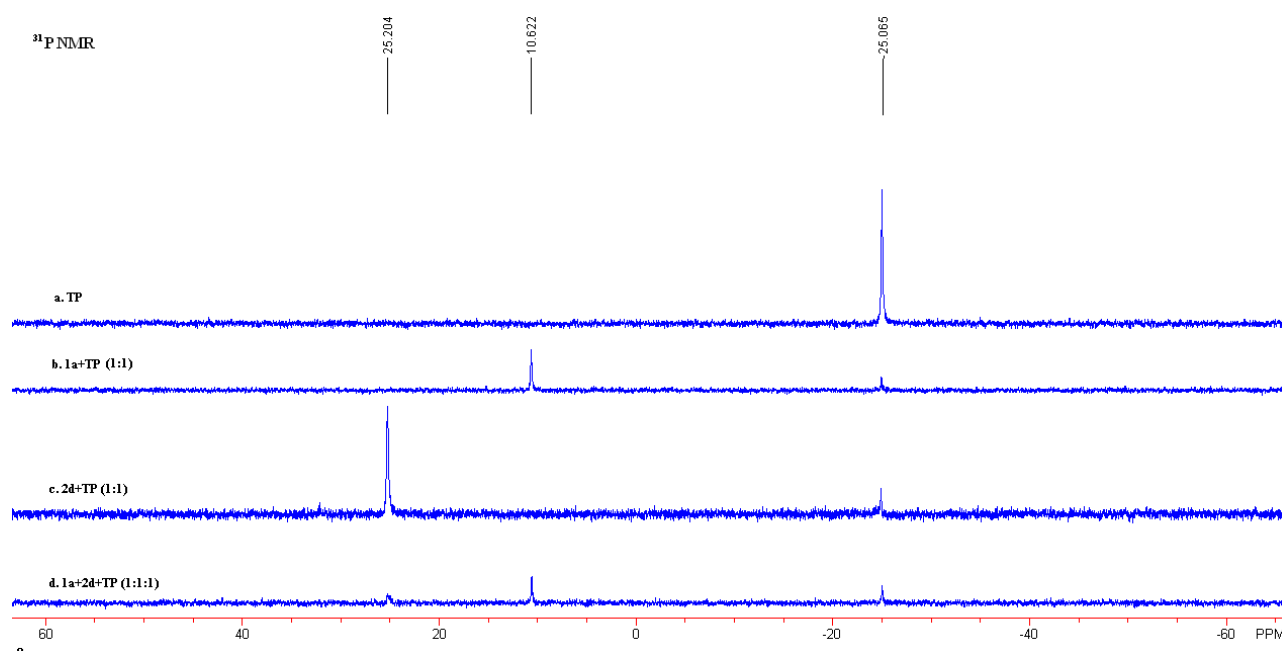


Figure SI-1. ^{31}P NMR Spectra (161.9 MHz, CDCl_3) of control experiments

4. References:

1. Deng, H.-P.; Wei, Y.; Shi, M. *Adv. Synth. Catal.* **2012**, 354, 783–789.
2. Plietker, B.; Niggemann, M. *Org. Lett.* **2003**, 5, 3353–3356.
3. Wurz, R. P.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, 127, 12234–12235.